Spring 5-31-2001

Structures, intramolecular rotation barriers, and thermodynamic properties of methane and ethylene carbons bonding to two unsaturated groups : ethylene, acetylene, phenyl and carbonyl

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ABSTRACT

STRUCTURES, INTRAMOLECULAR ROTATION BARRIERS, AND THERMODYNAMIC PROPERTIES OF METHANE AND ETHYLENE CARBONS BONDING TO TWO UNSATURATED GROUPS: ETHYLENE, ACETYLENE, PHENYL AND CARBONYL

by
Manish H. Gurbani

Enthalpy, $\Delta H_f\,^{\circ}_{298}$, entropy, S°_{298} and heat capacities $C_p(T)$ ($300 \leq T/K \leq 1500$) are determined for Methane, bi-phenyl (CCB2H2); Methane, phenyl-vinyl (CCBCDH2); Toluene, 1-formyl (CCBCOH2), Propyne, 3-phenyl (CCBCTH2); 1,4-pentadiene (CCD2H2); Propene, 3-formyl (CCDCOH2); Methane, di-formyl (CCO2H2); Propyne, 3-formyl (CCOCTH2); Methane, di-ethynl (CCT2H2); Ethene, bi-phenyl (CDCB2); 1,4 Butadiene, 3-phenyl (CDCBCD); Ethene, 1-ethynl-1-phenyl (CDCBCT); 1,4 Butadiene, 3-vinyl (CDCD2); 1,4 Butadiene, 2-ethynl (CDCDCT) and Ethene, 1,1-di-ethynl (CDCT2) using density functional B3LYP/6-31G(d) calculation method. Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d) density functional calculation level. Evaluation of data from the isodesmic reactions results in $\Delta H_f^{\circ}{}_{298}$ values for CCB2H2 of 42.41 kcal/mol, CCBCDH2 of 34.7 kcal/mol, CCBCOH2 of –13.35 kcal/mol, CCBCTH2 of 74.7 kcal/mol, CCD2H2 of 27.08 kcal/mol, CCDCOH2 of –20.68 kcal/mol, CCO2H2 of –64.88 kcal/mol, CCOCTH2 of 19.72 kcal/mol, CCT2H2 of 112.43 kcal/mol, CDCB2 of 60.86 kcal/mol, CDCBCD of 53.41 kcal/mol, CDCBCT of 94.96 kcal/mol, CDCD2 of 48.68 kcal/mol, CDCDCT of 85.45 kcal/mol and CDCT2 of 131.68 kcal/mol. Standard entropy (S°_{298}) and heat capacity ($C_p(T)$'s, $300 \leq T/K \leq 1500$) from vibrational, translational, and external rotational contributions are calculated using the rigid-rotor-harmonic-oscillator approximation

based on the vibration frequencies and structures obtained from the density functional studies. Potential energy as a function of internal rotation barrier is also determined using relaxed and non relaxed calculations using the B3LYP functional. Hindered internal rotational contributions to Entropy and Heat Capacity are calculated by the method of Pitzer and Gwinn. Groups for use in Benson type additivity estimations are determined. Enthalpy, entropy and $C_p(T)$ properties are determined for C/CB2/H2, C/CB/CD/H2, C/CB/CO/H2, C/CB/CT/H2, C/CD2/H2, C/CD/CO/H2, C/CO2/H2, C/CO/CT/H2, C/CT2/H2, CD/CB2, CD/CB/CD, CD/CB/CT, CD/CD2, CD/CD/CT, CD/CT2 groups for use in group additivity. Calculations result Group Values for C/CB2/H2 of –1.61 kcal/mol, C/CB/CD/H2 of –2.16 kcal/mol, C/CB/CO/H2 of –5.96 kcal/mol, C/CB/CT/H2 of –1.81kcal/mol, C/CD2/H2 of –2.62 kcal/mol, C/CD/CO/H2 of –6.13 kcal/mol, C/CO2/H2 of –6.08 kcal/mol, C/CO/CT/H2 of –5.38 kcal/mol, C/CT2/H2 of –3.43 kcal/mol, CD/CB2 of 10 kcal/mol, CD/CB/CD of 11.81 kcal/mol, CD/CB/CT of 11.3 kcal/mol, CD/CD2 of 12.19, CD/CD/CT of 11.05 kcal/mol, CD/CT2 of 15.22 kcal/mol.

STRUCTURES, INTRAMOLECULAR ROTATION BARRIERS, AND THERMODYNAMIC PROPERTIES OF METHANE AND ETHYLENE CARBONS BONDING TO TWO UNSATURATED GROUPS: ETHYLENE, ACETYLENE, PHENYL AND CARBONYL

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A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
In Partial Fulfillment of the Requirements for the Degree of
Master of Science in Chemical Engineering

Department of Chemical Engineering,
Chemistry and Environmental Science

May 2001

APPROVAL PAGE

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This thesis is dedicated to my family
for their unending love and encouragement.

ACKNOWLEDGMENT

I start by expressing my sincere appreciation to my advisor, Dr. Joseph Bozzelli, for his dedication, patience, and wisdom throughout the length of this study and the preparation of this thesis, and without whose guidance this research would not have been possible. I am grateful to Dr. Robert Pfeffer and Dr. Basil C Baltzis, who served as my committee members, for their inspirational and timely support, technical expertise, and acuity throughout the duration of the project.

I would also like to take this opportunity to thank Dr. Larry Lay for developing Vibir program and Mr. Chad Sheng for developing SMCps program. Vibir was very useful in calculating the Internal Rotation contribution to Entropy and Heat Capacity and SMCps was extremely useful in calculating the Translational, Vibrational, External Rotation contributions to Entropy and Heat Capacity. A special mention also has to be made of Mr. Jong Woo Lee and Mrs Hongyan Sun at New Jersey Institute of Technology for their help in this work and it's presentation.

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CHAPTER 1

INTRODUCTION

The importance of reliable and conveniently accessible thermochemical data (Enthalpies of Formation, Entropies, and Heat Capacities) is universally accepted among both scientists and engineers. This work is an attempt to provide thermochemical data for certain selected Hydrocarbons and Oxygenated Hydrocarbons, which are important intermediates in pyrolysis and thermal combustion processes. The species are also important in soot formation and low-pressure vapor deposition processes.[1]

The pyrolysis of light hydrocarbons such as methane, ethylene, acetylene or benzene is an important technical process. Chemical vapor deposition (CVD) or chemical vapor infiltration (CVI) are commonly used techniques to deposit materials with a large variety of functional and structural properties.[2-5] Depending on temperature, pressure and other conditions, the reaction may either lead to soot or, if the reaction co-ordinates are properly tuned, to products like improved carbon fibres, and other useful materials.[6]

However, despite the technical and industrial importance of CVD and CVI processes, comparatively little is known about the underlying chemical reactions that promote the formation of one material or the other.[1] The reaction system consists of virtually thousands of different elementary steps, all of which can be important at the high temperatures commonly employed in this field of material science.[1] Detailed information about the possible reaction mechanisms is, however, mandatory for a better understanding and a systematic improvement of existing synthetic strategies. Ultimately,

this knowledge may lead to the accelerated development of materials with desired properties. Furthermore, important information about the reverse process, i.e. carbon gasification reactions, may also be obtained.

It has been suggested that PACHs are precursors to soot in hydrocarbon flames.[7-9] and one area of uncertainty in these polycyclic aromatic systems concerns the fundamental thermodynamic properties and the kinetic behavior of PCAH formation and destruction, specifically as the temperature of varied pyrolysis, synthesis and combustion processes covers a wide range. An example of the limited level of understanding is that the influence of temperature, size, degree of ring condensation, etc. on individual PCAH stability is not quantitatively known or modeled. This is primarily due to the lack of requisite thermochemical properties of PCAHs.[10] It is, however, the molecules and intermediate stable species, which are an important part of the formation and synthesis processes, (precursors) that are a target of this study. We need to know the thermochemical properties of these species before we can model the formation and destruction of the polycyclics accurately.

Thermochemical property data on these precursor molecules are needed for evaluation of reaction paths and kinetic processes, including stability of intermediate adducts and prediction of final products. Thermochemical properties are also needed for use in kinetic modeling and in equilibrium codes. There is very little or no data on thermochemical properties of these species in the literature.[22,33,34,35,36] This thesis is an attempt to estimate fundamental thermochemical property data on a series of molecules which contain important chemical moieties – sp3 carbon structures (--CH2--) bonded to

two highly unsaturated groups and sp2 carbons (>C=CH2) bonded to two unsaturated groups. The unsaturated groups bonding to the Methane and Ethylene are Ethylene, Acetylene, Phenyl and Carbonyl.

During the past decade molecular electronic structure theory has evolved to the stage where it can provide critical information on structures, energetics and other properties that are difficult to obtain experimentally or are not accessible at all.[1] Especially with the progress in density functional theory (DFT) along with development of efficient algorithms and computer programs, molecular modeling has reached a reliability that allows for a description of molecular processes often with chemical accuracy. In this work the method is to use ab initio and moderate level Density Functional Computational chemistry on target molecules where enthalpy values can be determined to within a 1 to 2 kcal/mole.[16] Once the enthalpy of the target molecule is known, the target group is determined from known molecular values and the remaining known groups. Group values for use in group additivity have been calculated in order to construct (estimate) the thermochemical properties of larger molecule systems, where computational chemistry is not sufficiently accurate.

CHAPTER 2

STRUCTURES, INTRAMOLECULAR ROTATION BARRIERS, AND THERMODYNAMIC PROPERTIES OF METHANE AND ETHYLENE CARBONS BONDING TO TWO UNSATURATED GROUPS: ETHYLENE, ACETYLENE, PHENYL AND CARBONYL

2.1 Overview

Unsaturated Hydrocarbons and Oxygenated Hydrocarbons are important intermediates in pyrolysis, in combustion, in commercial thermal processes including soot formation as well as in low-pressure vapor deposition processes. Thermochemical property data on these species are important to understanding their stability, reaction paths and kinetics. Enthalpy, $\Delta H_f{}^{\circ}_{298;}$ entropy, S°_{298}; and Heat Capacities, $C_p(T)$ ($300 \leq T/K \leq 1500$); are determined for Methane, bi-phenyl (CCB2H2); Methane, phenyl-vinyl (CCBCDH2); Toluene, 1-formyl (CCBCOH2), Propyne, 3-phenyl (CCBCTH2); 1,4-pentadiene (CCD2H2); Propene, 3-formyl (CCDCOH2); Methane, di-formyl (CCO2H2); Propyne, 3-formyl (CCOCTH2); Methane, di-ethynl (CCT2H2); Ethene, bi-phenyl (CDCB2); 1,4 Butadiene, 3-phenyl (CDCBCD); Ethene, 1-ethynl-1-phenyl (CDCBCT); 1,4 Butadiene, 3-vinyl (CDCD2); 1,4 Butadiene, 2-ethynl (CDCDCT) and Ethene, 1,1-di-ethynl (CDCT2) using density functional calculation methods – moderate level computational chemistry.

Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d) density functional calculation level. Vibration frequencies are scaled for zero point energies and for thermal corrections. Enthalpies of formation ($\Delta H_f^{\circ}{}_{298}$) are determined using the $\Delta H^{\circ}_{rxn,298}$ with known enthalpies of other reactants and products in isodesmic reactions. Standard entropy (S°_{298}) and heat capacity ($C_p(T)$,$300 \leq T/K \leq 1500$)

from vibration, translation, and external rotational contributions are calculated using the rigid-rotor-harmonic-oscillator approximation based on the vibration frequencies and structures obtained from the density functional studies. Potential energy as a function of internal rotation barrier is determined using relaxed and non relaxed calculations using the B3LYP functional. Evaluation of data from the reactions results in $\Delta H_f^\circ{}_{298}$ values for CCB2H2 of 42.41 kcal/mol, CCBCDH2 of 34.7 kcal/mol, CCBCOH2 of –13.35 kcal/mol, CCBCTH2 of 74.7 kcal/mol, CCD2H2 of 27.08 kcal/mol, CCDCOH2 of –20.68 kcal/mol, CCO2H2 of – 64.88 kcal/mol, CCOCTH2 of 19.72 kcal/mol, CCT2H2 of 112.43 kcal/mol, CDCB2 of 60.86 kcal/mol, CDCBCD of 53.41 kcal/mol, CDCBCT of 94.96 kcal/mol, CDCD2 of 48.68 kcal/mol, CDCDCT of 85.45 kcal/mol and CDCT2 of 131.68 kcal/mol.

Groups for use in Benson type additivity estimation schemes are of value because they can allow accurate estimation of much larger molecules, where ab initio or density functional computational chemistry can not be used. Enthalpy, Entropy and $C_p(T)$ properties are determined for two series of target groups in this study. The first series comprises unsaturated moieties bonded to methylene (–CH2--) C/CB2/H2, C/CB/CD/H2, C/CB/CO/H2, C/CB/CT/H2, C/CD2/H2, C/CD/CO/H2, C/CO2/H2, C/CO/CT/H2, C/CT2/H2. The second series of groups developed in this work are for unsaturated moieties bonded to the sp2 hybridized carbon (ethylene, >C=CH2): CD/CB2, CD/CB/CD, CD/CB/CT, CD/CD2, CD/CD/CT, CD/CT2 groups. Calculations result in Group Values for C/CB2/H2 of –1.61 kcal/mol, C/CB/CD/H2 of –2.16 kcal/mol, C/CB/CO/H2 of –5.96 kcal/mol, C/CB/CT/H2 of –1.81kcal/mol, C/CD2/H2 of –2.62 kcal/mol, C/CD/CO/H2 of –6.13 kcal/mol, C/CO2/H2 of –6.08 kcal/mol, C/CO/CT/H2 of

–5.38 kcal/mol, C/CT2/H2 of –3.43 kcal/mol, CD/CB2 of 10 kcal/mol, CD/CB/CD of 11.81 kcal/mol, CD/CB/CT of 11.3 kcal/mol, CD/CD2 of 12.19, CD/CD/CT of 11.05 kcal/mol, CD/CT2 of 15.22 kcal/mol. Group values determined in this work show reasonable agreement with literature values; but only a limited number of literature values are available for comparison. Reasonable agreement between the calculated and previously reported values suggests that the use of isodesmic reaction analysis results in effective cancellation of errors and thus accurate enthalpy values.

2.2 Background

The molecules studied in this work are specifically selected because of their relevance to formation and destruction processes in pyrolysis, vapor deposition, soot and carbon black formation and in combustion. Unsaturated hydrocarbons and qxygenated hydrocarbons are important intermediates in pyrolysis and combustion thermal processes including soot formation as well as in low-pressure vapor deposition processes. Thermochemical property data on these species are important to understanding their stability, reaction paths. and kinetics. Knowledge of the thermodynamic parameters for these species is central to understanding and predicting reaction pathways, rate constants and equilibrium constants. There is little or no experimental studies on the thermodynamic properties of these species, probably due (at least in part) to the difficulty in synthesis of pure compounds.

In this work, enthalpy, $\Delta H_f^{\circ}{}_{298}$, entropy, $S^{\circ}{}_{298}$ and heat capacities $C_p(T)$ are determined for the target species using density functional calculation methods. Enthalpies of formation are evaluated at B3LYP/6-31G(d) calculation level, using

working reactions for a high level of accuracy in the enthalpy values. The working reactions used are isodesmic, that is they have bond balance on both sides of the reaction for effective cancellation of errors.

Enthalpies of formation for the target species are estimated using total energies from the B3LYP calculations and isodesmic reactions. The B3LYP Density functional and ab initio calculations with ZPVE and thermal correction are performed for all four compounds in each reaction, and enthalpy of reaction $\Delta H^{o}_{rxn,298}$ is calculated. Since enthalpy of formation of three compounds, have been experimentally determined or theoretical calculated, the unknown enthalpy of formation of target compound is obtained.

As an example, the following formula illustrates the calculation of $\Delta H_f^{o}{}_{298}$(CCBCDH2) for a given level of calculation:

$$\Delta H^{o}_{rxn,298} = E_{298}(C7H8) + E_{298}(C4H6) - E_{298}(CCBCDH2) - E_{298}(C2H4)$$

$$\Delta H_f^{o}{}_{298}(CCBCDH2) = \Delta H_f^{o}{}_{298}(C7H8) + \Delta H_f^{o}{}_{298}(C4H6) - \Delta H_f^{o}{}_{298}(C2H4) - \Delta H^{o}_{rxn,298}$$

The enthalpies of formation ($\Delta H_f^{o}{}_{298}$) and their respective uncertainties for standard species used in the working reactions.

Contributions to Entropy and Heat Capacity from Internal Rotation also need to be evaluated. They are estimated using calculated barriers to internal rotation about the CH2—Cd, CH2—Ct, CH2—Cb and CH2—C=O single bonds, and foldness of the intramolecular rotation using the method of Pitzer and Gwinn.[17] Rotation barriers are determined with relaxed (fully optimized) and non-relaxed (scan mode in Gaussian where other rotors structure properties are held rigid) and the use of B3LYP density functional calculations.

2.3 Computational Methods

2.3.1 Selection of Method

All ab initio calculations are performed using the Gaussian 94 and Gaussian 98 program suites.[18] The structural parameters are fully optimized at the B3LYP/6-31g(d) level of theory. Harmonic vibration frequencies and zero-point vibrational energies (ZPVE) are computed at the same level. The optimized geometrical parameters are used to obtain total electronic energies in the B3LYP/6-31G(d) single point calculations.[19-21]

B3LYP/6-31G(d) is chosen because it is commonly used and is reported to yield accurate geometries and reasonable energies.[22,23] Durant[21,23] has compared density functional calculations B3LYP and hybrid (BH and H) with MP2 and Hartree-Fock methods for geometry and vibration frequencies. He reports that these density functional methods provide excellent geometries and vibration frequencies, relative to MP2 at a reduced computational expense. Petersson et al.[24] currently recommends use of B3LYP for geometry and frequencies in several of his CBS calculation methods. Comparison of calculation results from B3LYP/6-31G(d) with use of working reactions for $\Delta H_f\,^{o}_{298}$, against data from higher calculation levels will provide some calibration of the B3LYP/6-31G(d) values for larger molecules where this may be one of the few available calculation methods (with similar working reactions). The geometry is obtained at the B3LYP/6-31G(d) level of theory, while the ZPE used is the scaled (by 0.9806) HF/6-31G value.

2.3.2 Enthalpies of Formation ($\Delta H_f{}^\circ_{298}$)

Enthalpies of formation ($\Delta H_f{}^\circ_{298}$) for the species are estimated using total energies obtained by the B3LYP/6-31G(d) and isodesmic reactions. Total energies are corrected by zero-point vibration energies (ZPVE) which are scaled by 0.9806 as recommended by Scott et al.[25] Thermal correction, 0 K to 298.15 K, is calculated to estimate $\Delta H_f{}^\circ_{298}$ at 298.15 K.[26]

The method of isodesmic reactions relies on the similarity of the bonding environments in the reactants and products that leads to partial cancellation of systematic errors in the density functional and ab initio molecular orbital calculations.[26] Reactions selected to determine $\Delta H_f{}^\circ_{298}$ of each species are represented in Table 2.32. The basic requirement of an isodesmic reaction is that the number of each type of bond is conserved in the reaction; this leads to an accurate cancellation of error on both sides of a reaction and results in an accurate calculated enthalpy of reaction. This enthalpy of reaction is then used, in conjunction with the enthalpy of formation of the three standard molecules in the working reaction to find the enthalpy of formation on the target molecule. Density functional and ab initio calculations with ZPVE and thermal correction are performed for all four compounds in each reaction, and enthalpy of reaction $\Delta H^\circ_{rxn,298}$ is calculated. Since accurate enthalpies of formation of the three standard compounds, have been experimentally determined or theoretically calculated, along with the enthalpy of reaction, the unknown enthalpy of the target compound is obtained. The Density functional and ab initio calculations are performed on the most stable conformer of each compound, and the $\Delta H_f{}^\circ_{298}$ of this conformer is calculated using isodesmic reactions.

Corrections have not been made to the $\Delta H_f\,^{\circ}_{298}$ for each species to include other conformers beside the lowest energy conformer.

2.3.3 Entropy (S°_{298}) and Heat Capacities ($C_p(T)$'s, $300 \leq T/K \leq 1500$)) and Hindered Rotation Contribution to Thermodynamic Parameters

Entropies S°_{298} and heat capacities ($C_p(T)$'s, $300 \leq T/K \leq 1500$) are calculated using the rigid-rotor-harmonic-oscillator approximation based on frequencies and moments of inertia of the optimized B3LYP/6-31G(d) structures. Calculated Entropies are for the lowest Energy, most stable conformer and corrections have not been made for higher energy conformers. Contributions to entropy and heat capacity from internal rotation are estimated using the B3LYP determined barriers and foldness of the intramolecular rotation and the method of Pitzer and Gwinn[17]. Rotation barriers are determined with the B3LYP calculations. Potential energy as a function of internal rotation barrier is determined using relaxed and non relaxed calculations at using the B3LYP functional. Potential barriers for internal rotation are calculated at the B3LYP/6-31G(d) level, relaxed scan (optimized) for CCBCTH2 and CCD2H2; B3LYP/6-31G(d) with rigid scan for CDCBCT; B3LYP/6-31G(d,p) relaxed scan (optimized) for CCO2H2, CDCD2; B3LYP/6-31G(d,p) with rigid scan for CCBCOH2, CCOCTH2; B3LYP/6-31+G(d,p) relaxed scan (optimized) for CCDCOH2; B3LYP/3-21G relaxed scan (optimized) for CCB2H2, CCBCDH2, CDCB2, CDCBCD, CDCDCT.

2.4 Results and Discussion

2.4.1 Geometries and Vibrational Frequencies

The fully optimized geometries at the B3LYP/6-31g(d) density functional calculation level for the species are presented in Figures 2.1 to 2.15. Numerical values of the optimized structural parameters including carbon-hydrogen, carbon-oxygen, oxygen-oxygen, oxygen-hydrogen bond distances along with applicable bond angles and dihedral (twist) angles are listed in Tables 2.1 to 2.15.

Table 2.1 Structure Parameters [a,b] for CCB2H2

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	C	1.39			1		
3	C	1.40	120.24		2	1	
4	C	1.39	119.48	-0.01	3	2	1
5	C	1.40	120.08	0.05	4	3	2
6	C	1.40	120.83	-0.15	1	2	3
7	C	1.52	120.85	-178.58	6	1	2
8	C	1.52	114.71	-53.12	7	6	1
9	C	1.40	120.61	-61.27	8	7	6
10	C	1.39	120.86	-179.42	9	8	7
11	C	1.40	120.21	-0.13	10	9	8
12	C	1.39	119.51	0.01	11	10	9
13	C	1.40	121.01	-179.58	8	7	9
14	H	1.09	119.77	179.39	1	2	3
15	H	1.09	119.70	179.96	2	1	6
16	H	1.09	120.24	-179.89	3	2	1
17	H	1.09	120.18	-179.82	4	3	2
18	H	1.09	119.63	179.89	5	4	3
19	H	1.10	109.30	69.18	7	6	1
20	H	1.10	108.55	-175.83	7	6	1
21	H	1.09	119.35	0.97	9	8	7
22	H	1.09	119.74	179.89	10	9	8
23	H	1.09	120.22	-179.96	11	10	9
24	H	1.09	120.18	-179.96	12	11	10
25	H	1.09	119.38	-0.25	13	8	7

[a]Distances in Angstroms and Angles in Degrees.

[b]Geometry Parameters optimized at the B3LYP/6-31g(d) level of theory.

[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

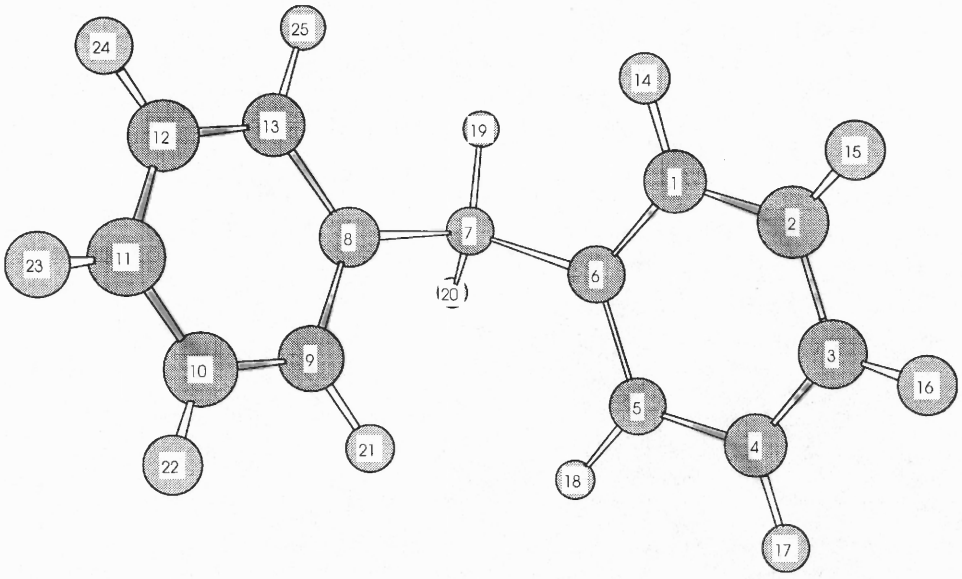


Figure 2.1 B3LYP/6-31G(d) optimized geometry of CCB2H2. See Table 2.1 for structure parameters.

Table 2.2 Structure Parameters [a,b] for CCBCDH2

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	C	1.39			1		
3	C	1.40	120.21		2	1	
4	C	1.39	119.51	-0.02	3	2	1
5	C	1.40	120.08	0.07	4	3	2
6	C	1.40	120.81	-0.20	1	2	3
7	C	1.52	120.58	-179.09	6	1	2
8	C	1.51	113.47	-54.09	7	6	1
9	C	1.33	124.96	121.83	8	7	6
10	H	1.09	119.95	179.41	1	2	3
11	H	1.09	119.75	179.92	2	1	6
12	H	1.09	120.23	-179.90	3	2	1
13	H	1.09	120.15	-179.82	4	3	2
14	H	1.09	119.66	179.96	5	4	3
15	H	1.10	108.56	-121.79	7	6	8
16	H	1.10	109.88	-115.92	7	6	15
17	H	1.09	115.61	-57.73	8	7	6
18	H	1.09	121.80	179.78	9	8	7
19	H	1.09	121.67	0.15	9	8	7

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

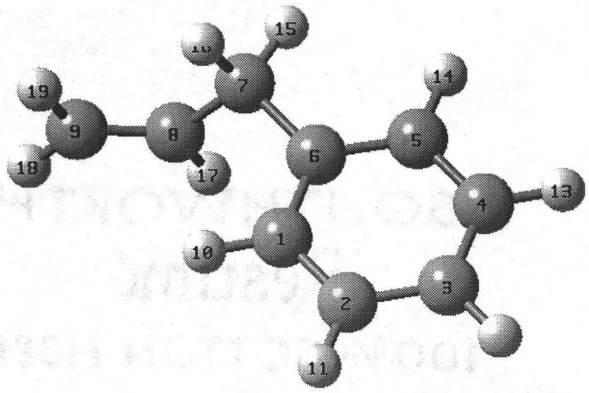


Figure 2.2 B3LYP/6-31G(d) Optimized Geometry of CCBCDH2. See Table 2.2 for Structure Parameters.

Table 2.3 Structure Parameters [a,b] for CCBCOH2

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	C	1.52			1		
3	O	1.21	124.46		2	1	
4	H	1.11	114.47	178.90	2	1	3
5	C	1.52	110.74	-120.95	1	2	3
6	H	1.09	111.97	-120.52	1	5	2
7	H	1.10	109.83	119.06	1	5	2
8	C	1.40	119.93	74.43	5	1	2
9	H	1.09	119.42	1.66	8	5	1
10	C	1.39	120.67	179.88	8	5	9
11	H	1.09	119.75	0.19	10	8	9
12	C	1.40	120.11	180.00	10	11	8
13	H	1.09	120.17	0.08	12	10	11
14	C	1.40	120.18	-179.88	12	13	10
15	H	1.09	120.15	0.05	14	12	13
16	C	1.40	119.74	-179.80	14	15	12
17	H	1.09	119.72	0.18	16	14	15

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

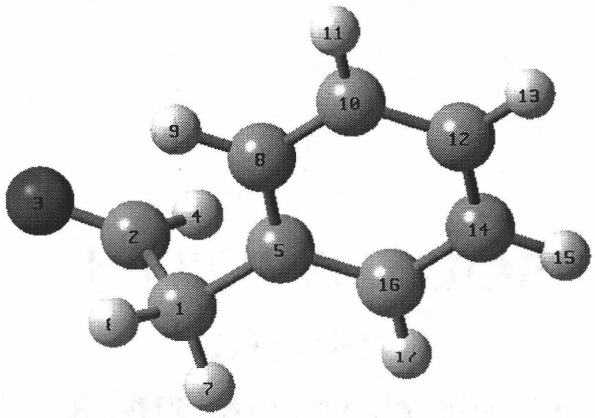


Figure 2.3 B3LYP/6-31G(d) optimized geometry of CCBCOH2. See Table 2.3 for structure parameters.

Table 2.4 Structure Parameters [a,b] for CCBCTH2

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	C	1.40			1		
3	C	1.39	120.36		2	1	
4	C	1.40	119.48	0.05	3	2	1
5	C	1.39	120.08	-0.01	4	3	2
6	C	1.40	120.49	0.00	1	2	3
7	C	1.53	122.54	178.77	6	1	2
8	C	1.46	115.81	11.33	7	6	1
9	C	1.21	179.16	-170.61	8	7	6
10	H	1.09	120.19	-179.69	1	2	3
11	H	1.09	119.55	179.90	2	1	6
12	H	1.09	120.31	179.90	3	2	1
13	H	1.09	120.16	179.79	4	3	2
14	H	1.09	119.68	179.85	5	4	3
15	H	1.10	108.83	-122.63	7	6	8
16	H	1.10	108.90	123.04	7	6	8
17	H	1.07	179.75	-145.45	9	8	15

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

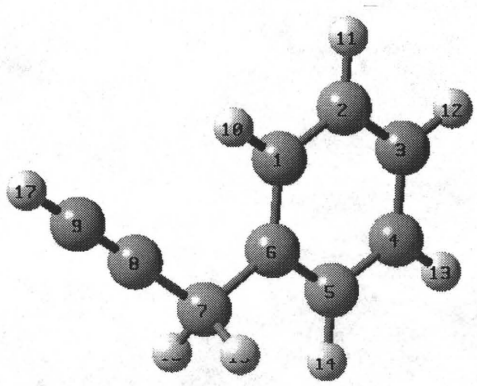


Figure 2.4 B3LYP/6-31G(d) optimized geometry of CCBCTH2. See Table 2.4 for structure parameters.

Table 2.5 Structure Parameters [a,b] for CCD2H2

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	H	1.10			1		
3	H	1.10	107.00		1	2	
4	C	1.51	108.97	-118.65	1	2	3
5	C	1.51	112.18	121.79	1	4	2
6	C	1.33	125.05	118.22	4	1	5
7	H	1.09	121.81	-179.62	6	4	1
8	H	1.09	121.68	0.67	6	4	1
9	C	1.33	125.06	118.26	5	1	4
10	H	1.09	121.81	-179.64	9	5	1
11	H	1.09	121.69	-179.69	9	5	10
12	H	1.09	115.45	-60.79	4	1	5
13	H	1.09	119.49	179.65	5	9	11

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

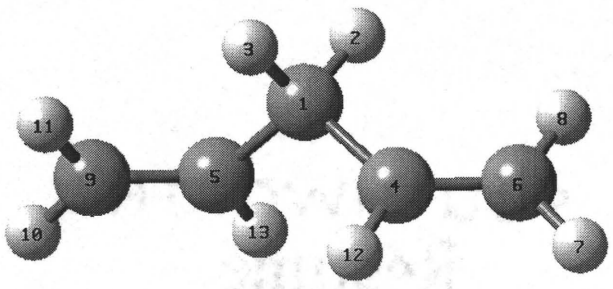


Figure 2.5 B3LYP/6-31G(d) optimized geometry of CCD2H2. See Table 2.5 for structure parameters.

Table 2.6 Structure Parameters [a,b] for CCDCOH2

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	C	1.51			1		
3	C	1.33	124.84		2	1	
4	H	1.09	121.61	178.72	3	2	1
5	H	1.09	121.85	-1.98	3	2	1
6	H	1.09	119.49	0.65	2	3	4
7	C	1.52	110.88	70.09	1	2	6
8	H	1.10	111.84	-120.42	1	2	7
9	H	1.10	109.64	-120.76	1	2	8
10	O	1.21	124.66	-119.68	7	1	2
11	H	1.11	114.19	179.24	7	1	10

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

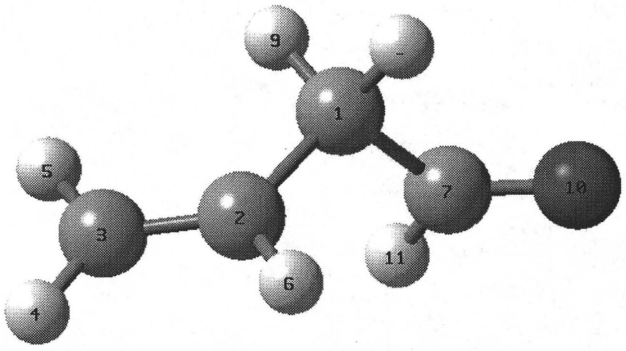


Figure 2.6 B3LYP/6-31G(d) optimized geometry of CCDCOH2. See Table 2.6 for structure parameters.

Table 2.7 Structure Parameters [a,b] for CCO2H2

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	C	1.52	1.00				
3	C	1.52	114.01	1.00	2		
4	O	1.21	124.41	-4.71	3	1	2
5	O	1.21	123.11	-136.95	2	1	3
6	H	1.10	109.86	124.53	1	2	3
7	H	1.10	108.82	-119.67	1	2	3
8	H	1.11	115.38	42.08	2	1	4
9	H	1.11	114.65	175.50	3	1	2

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

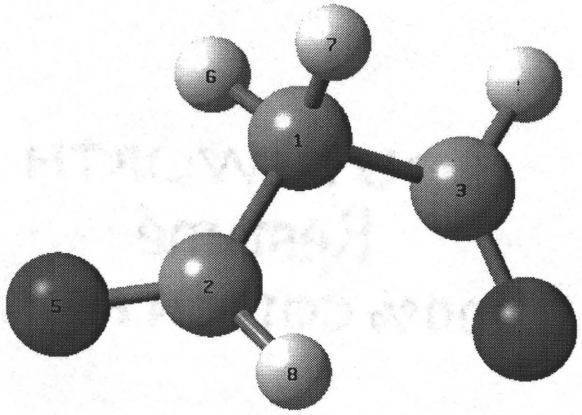


Figure 2.7 B3LYP/6-31G(d) optimized geometry of CCO2H2. See Table 2.7 for structure parameters.

Table 2.8 Structure Parameters [a,b] for CCOCTH2

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	C	1.53			1		
3	O	1.21	123.07		2	1	
4	H	1.11	121.89	-178.63	2	3	1
5	C	1.46	112.88	-32.45	1	2	4
6	H	1.10	106.70	121.01	1	2	5
7	H	1.10	108.07	-124.72	1	2	5
8	C	1.21	151.73	176.11	5	6	1
9	H	1.07	161.74	-178.04	8	6	5

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

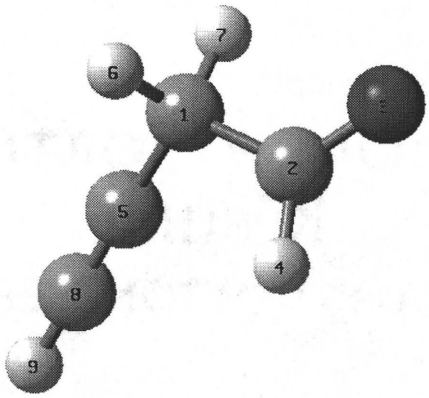


Figure 2.8 B3LYP/6-31G(d) optimized geometry of CCOCTH2. See Table 2.8 for structure parameters.

Table 2.9 Structure Parameters [a,b] for CCT2H2

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	C	1.47	1.00				
3	C	1.47	113.65	1.00	2		
4	H	1.10	109.33	122.46	1	2	3
5	H	1.10	109.33	-122.46	1	2	3
6	C	1.21	150.26	179.32	2	4	1
7	C	1.21	150.24	179.38	3	5	1
8	H	1.07	179.74	123.03	6	2	4
9	H	1.07	179.75	123.60	7	3	5

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

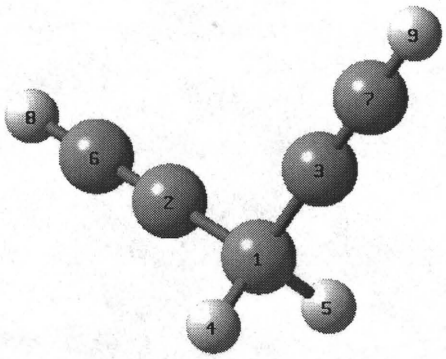


Figure 2.9 B3LYP/6-31G(d) optimized geometry of CCT2H2. See Table 2.9 for structure parameters.

Table 2.10 Structure Parameters [a,b] for CDCB2

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	C	1.35			1		
3	H	1.09	121.58		1	2	
4	H	1.09	121.59	-180.00	1	2	3
5	C	1.49	120.63	-3.41	2	1	3
6	C	1.41	120.95	139.80	5	2	1
7	C	1.39	120.88	-177.55	6	5	2
8	C	1.40	120.28	-0.57	7	6	5
9	C	1.40	119.49	-0.12	8	7	6
10	C	1.41	120.87	-178.58	5	2	6
11	H	1.09	119.12	-3.55	10	5	2
12	H	1.09	120.12	-179.08	9	8	7
13	H	1.09	120.25	-179.62	8	7	6
14	H	1.09	119.63	179.34	7	6	5
15	H	1.09	119.36	1.66	6	5	2
16	C	1.49	120.64	176.59	2	1	3
17	C	1.41	120.95	139.82	16	2	1
18	C	1.39	120.88	-177.54	17	16	2
19	C	1.40	120.28	-0.57	18	17	16
20	C	1.40	119.49	-0.11	19	18	17
21	C	1.41	120.87	-178.58	16	2	17
22	H	1.09	119.12	-3.56	21	16	2
23	H	1.09	120.12	-179.08	20	19	18
24	H	1.09	120.25	-179.62	19	18	17
25	H	1.09	119.63	179.34	18	17	16
26	H	1.09	119.36	1.66	17	16	2

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

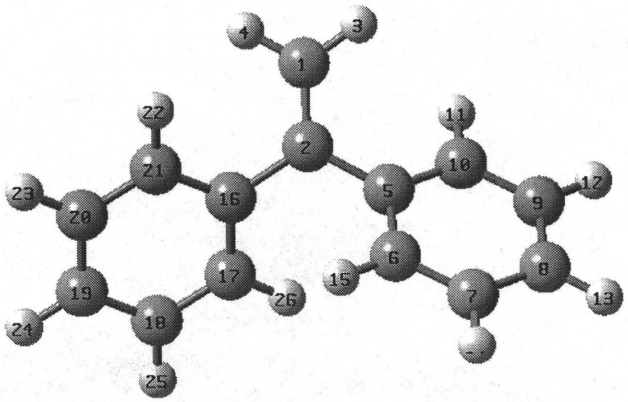


Figure 2.10 B3LYP/6-31G(d) optimized geometry of CDCB2. See Table 2.10 for structure parameters.

Table 2.11 Structure Parameters [a,b] for CDCBCD

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	C	1.35			1		
3	H	1.09	121.86		2	1	
4	H	1.09	121.21	179.71	2	1	3
5	C	1.49	121.86	4.44	1	2	3
6	C	1.41	121.46	32.87	5	1	2
7	C	1.39	120.94	-179.02	6	5	1
8	C	1.40	120.26	-0.45	7	6	5
9	C	1.40	119.49	-0.14	8	7	6
10	C	1.39	120.20	0.16	9	8	7
11	H	1.09	119.29	0.31	10	5	1
12	H	1.09	120.12	180.00	9	8	7
13	H	1.09	120.24	-179.68	8	7	6
14	H	1.09	119.66	-179.66	7	6	5
15	H	1.09	119.29	2.49	6	5	1
16	C	1.48	121.08	-176.08	1	2	3
17	C	1.34	125.26	38.74	16	1	2
18	H	1.09	121.40	-178.01	17	16	1
19	H	1.09	121.73	2.50	17	16	1
20	H	1.09	115.82	-142.17	16	1	2

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

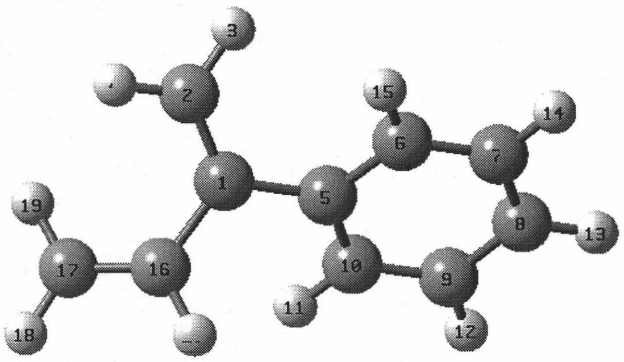


Figure 2.11 B3LYP/6-31G(d) optimized geometry of CDCBCD. See Table 2.11 for structure parameters.

Table 2.12 Structure Parameters [a,b] for CDCBCT

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	C	1.35			1		
3	C	1.44	119.19		1	2	
4	C	1.49	123.25	-179.24	1	2	3
5	C	1.40	120.51	154.07	4	1	2
6	C	1.39	120.80	-178.48	5	4	1
7	C	1.40	120.29	-0.56	6	5	4
8	C	1.40	119.46	-0.30	7	6	5
9	C	1.41	121.13	-179.79	4	1	5
10	C	1.21	179.28	174.33	3	1	2
11	H	1.08	121.03	-1.67	2	1	3
12	H	1.08	121.64	177.30	2	1	3
13	H	1.09	119.21	1.13	5	4	1
14	H	1.09	119.58	179.56	6	5	4
15	H	1.09	120.31	-179.69	7	6	5
16	H	1.09	120.11	-178.83	8	7	6
17	H	1.09	119.71	-3.10	9	4	1
18	H	1.07	179.14	25.10	10	3	2

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

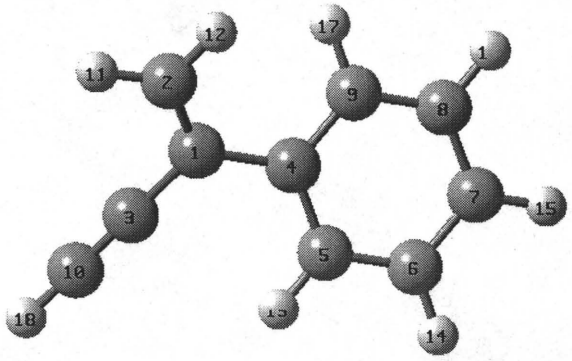


Figure 2.12 B3LYP/6-31G(d) optimized geometry of CDCBCT. See Table 2.12 for structure parameters.

Table 2.13 Structure Parameters [a,b] for CDCD2

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	NA	NB	NC
1	C						
2	C	1.35	1.00				
3	H	1.09	121.35	2	1		
4	H	1.09	121.67	179.42461	2	1	3
5	C	1.48	121.36	178.96216	1	2	3
6	H	1.09	115.95	139.42916	5	1	2
7	C	1.34	125.15	-40.8883	5	1	2
8	H	1.09	121.80	-2.4857	7	5	1
9	H	1.09	121.39	178.12109	7	5	1
10	C	1.47	119.87	-2.40	1	2	3
11	H	1.09	115.05	-5.99	10	1	2
12	C	1.34	126.15	179.59	10	1	11
13	H	1.09	121.12	179.89	12	10	1
14	H	1.09	122.41	-0.85	12	10	1

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

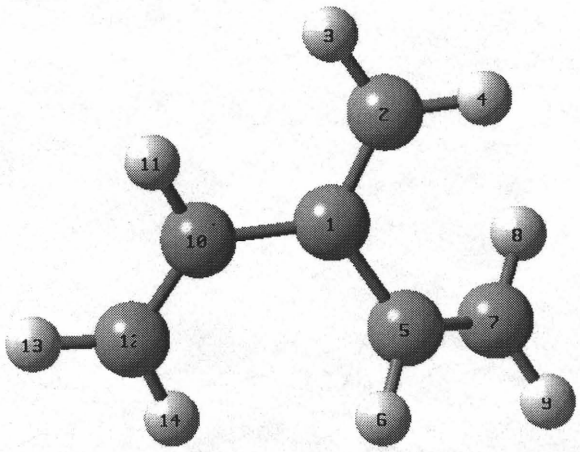


Figure 2.13 B3LYP/6-31G(d) optimized geometry of CDCD2. See Table 2.13 for structure parameters.

Table 2.14 Structure Parameters [a,b] for CDCDCT

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	C	1.35	1.00				
3	C	1.47	121.12	2	1		
4	C	1.34	125.48	179.99117	3	2	1
5	C	1.43	120.34	-179.98452	2	1	3
6	C	1.21	152.09	179.98978	5	1	2
7	H	1.09	120.83	-179.98646	1	2	5
8	H	1.08	121.73	179.98957	1	2	3
9	H	1.09	121.61	0.00438	4	3	2
10	H	1.09	121.17	-179.99	4	3	2
11	H	1.07	160.39	-179.97	6	1	2
12	H	1.09	119.86	179.99	3	4	2

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

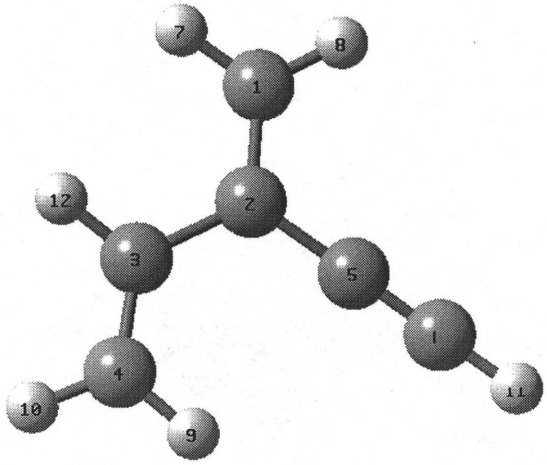


Figure 2.14 B3LYP/6-31G(d) optimized geometry of CDCDCT. See Table 2.14 for structure parameters.

Table 2.15 Structure Parameters [a,b] for CDCT2

Atom Number (I)	Chemical Symbol	Bond Length NA : I	Bond Angle NB : NA : I	Dihedral Angle NC : NB : NA : I	Connecting Atoms NA	NB	NC
1	C						
2	C	1.35	1.00				
3	H	1.08	120.82	1	2		
4	H	1.08	120.82	180	1	2	3
5	C	1.44	121.63	180	2	1	3
6	C	1.21	152.95	0	5	1	4
7	H	1.07	161.58	0	6	1	4
8	C	1.44	121.63	0	2	1	3
9	C	1.21	152.95	0	8	1	3
10	H	1.07	161.58	0.00	9	1	3

[a]Distances in Angstroms and Angles in Degrees.
[b]Structure Parameters Optimized at the B3LYP/6-31g(d) level of theory.
[c]Connecting Atoms indicates the Atoms used to indicate the relative position of the Atom shown under Atom Number.

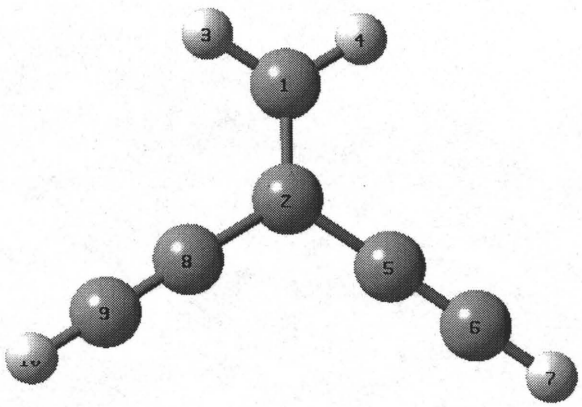


Figure 2.15 B3LYP/6-31G(d) optimized geometry of CDCT2. See Table 2.15 for structure parameters.

Harmonic vibrational frequencies are calculated for the species at the B3LYP/6-31G(d) level of theory on the basis of optimized geometries at the same level of theory. The unscaled vibrational frequencies and moments of inertia for the species are given in Tables 2.16 to 2.30 and 2.31 respectively. In Tables 2.16 to 2.30, the two lowest frequencies (corresponding to torsional motions) are omitted in calculation of entropies S^{o}_{298} and heat capacities $C_p(T)$, but their contributions have been replaced with values from analysis of the internal rotations (see Table 2.64).

Table 2.16 Vibration Frequencies [a,b] (cm^{-1}) for CCB2H2

24.14	26.21	66.05
195.13	226.91	290.39
344.53	416.98	417.74
462.71	483.01	565.19
623.73	635.21	637.64
712.22	716.53	752.49
754.81	833.20	837.34
861.00	861.67	908.39
931.06	954.55	966.44
967.13	994.35	994.42
1018.50	1018.79	1058.60
1059.80	1107.23	1117.17
1192.05	1192.39	1212.42
1214.15	1214.98	1221.53
1231.84	1321.09	1362.34
1364.94	1373.13	1382.76
1499.47	1500.16	1513.33
1546.00	1547.40	1642.21
1646.24	1662.32	1667.37
3033.40	3066.99	3172.51
3173.06	3178.41	3179.81
3188.27	3188.94	3196.35
3196.88	3207.74	3208.28

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.17 Vibration Frequencies [a,b] (cm^{-1}) for CCBCDH2

26.35	85.23	147.21
274.93	330.53	399.91
417.74	498.08	538.51
635.68	668.54	715.78
758.05	834.65	862.13
913.76	934.10	940.29
951.70	967.45	994.56
1018.47	1037.26	1059.21
1109.30	1136.97	1192.06
1214.07	1221.26	1248.01
1322.68	1339.14	1363.46
1375.61	1472.27	1498.87
1507.52	1546.22	1644.21
1664.49	1728.50	3026.45
3061.24	3148.98	3158.15
3172.82	3179.64	3189.36
3197.26	3208.43	3235.23

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.18 Vibration Frequencies [a,b] (cm^{-1}) for CCBCOH2

29.31	52.79	142.85
292.34	322.71	416.76
449.11	519.61	577.49
635.52	715.48	765.82
780.37	858.43	862.43
923.17	968.66	998.34
1013.20	1020.87	1058.00
1063.57	1117.89	1193.62
1205.79	1215.67	1225.23
1308.50	1358.55	1370.54
1433.48	1492.17	1502.14
1545.54	1644.12	1663.20
1831.82	2910.79	3046.27
3115.73	3177.24	3181.60
3191.27	3200.39	3211.34

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.19 Vibration Frequencies [a,b] (cm^{-1}) for CCBCTH2

15.35	130.73	196.06
312.16	332.37	416.28
424.17	472.22	594.78
610.01	632.58	635.03
709.80	744.83	806.24
862.80	905.72	967.65
974.54	978.53	998.87
1019.41	1059.96	1113.47
1192.61	1209.11	1215.94
1251.09	1313.92	1366.45
1379.26	1493.27	1501.83
1546.85	1646.58	1665.89
2242.86	3018.85	3048.09
3170.00	3183.14	3193.68
3205.80	3213.46	3495.13

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.20 Vibration Frequencies [a,b] (cm^{-1}) for CCD2H2

90.66	104.62	299.65
372.81	454.35	614.77
679.80	906.15	918.64
941.45	942.54	972.51
1037.13	1039.32	1094.49
1179.66	1275.86	1319.53
1332.80	1346.12	1470.63
1472.67	1502.55	1722.09
1736.19	3022.52	3061.07
3148.48	3149.01	3158.03
3158.63	3234.86	3234.98

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.21 Vibration Frequencies [a,b] (cm^{-1}) for CCDCOH2

62.13	86.84	312.57
394.02	502.64	649.44
814.73	946.04	952.01
973.20	1037.65	1066.15
1150.02	1255.98	1301.06
1339.29	1430.64	1469.31
1489.36	1724.52	1836.13
2909.63	3039.40	3107.15
3157.14	3164.50	3240.90

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.22 Vibration Frequencies [a,b] (cm^{-1}) for CCO2H2

26.24	95.55	232.14
462.30	640.45	699.28
860.84	922.33	1067.75
1098.45	1226.14	1324.61
1431.87	1439.06	1454.85
1828.50	1841.35	2921.36
2974.88	3014.35	3094.05

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.23 Vibration Frequencies [a,b] (cm^{-1}) for CCOCTH2

53.93	174.13	330.55
462.86	507.82	609.47
635.63	732.09	984.80
1036.73	1051.32	1230.64
1307.95	1427.67	1468.56
1841.14	2245.76	2942.24
3016.11	3094.32	3494.33

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.24 Vibration Frequencies [a,b] (cm^{-1}) for CCT2H2

138.17	313.88	329.84
340.86	558.42	604.55
605.65	628.32	631.12
908.51	953.55	1003.76
1254.00	1359.96	1486.12
2247.74	2253.56	3019.08
3044.57	3494.88	3495.45

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.25 Vibration Frequencies [a,b] (cm^{-1}) for CDCB2

45.63	63.41	81.59
142.93	220.06	236.89
296.38	345.12	419.61
423.52	449.23	461.94
579.65	603.39	629.44
634.87	655.77	705.71
714.53	726.69	738.99
791.94	801.93	850.54
862.98	865.19	919.23
936.87	937.88	972.48
974.00	996.75	997.22
1017.37	1017.42	1056.25
1058.18	1097.63	1114.24
1120.26	1179.57	1192.91
1193.14	1215.60	1217.12
1319.56	1339.61	1357.18
1367.00	1367.93	1456.32
1490.76	1493.72	1542.02
1545.30	1631.84	1633.21
1659.51	1661.52	1681.65
3174.01	3180.86	3181.44
3188.96	3189.11	3200.04
3200.22	3206.80	3207.31
3212.29	3212.63	3254.77

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.26 Vibration Frequencies [a,b] (cm^{-1}) for CDCBCD

62.74	106.08	132.51
227.97	295.03	350.75
383.03	420.22	470.95
527.04	628.41	638.42
693.56	717.92	760.05
776.21	796.81	863.63
911.99	926.07	936.58
944.97	972.37	997.19
1017.46	1037.00	1057.13
1100.12	1111.40	1129.84
1193.16	1217.01	1298.85
1333.74	1349.83	1368.22
1455.17	1474.17	1494.72
1544.71	1633.44	1661.90
1678.73	1711.09	3151.69
3167.52	3175.41	3180.39
3187.79	3198.26	3204.42
3211.34	3247.01	3256.75

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.27 Vibration Frequencies [a,b] (cm^{-1}) for CDCBCT

45.41	122.84	161.50
257.87	301.59	401.85
417.42	422.32	483.73
574.99	612.59	630.75
634.04	651.56	706.19
733.78	743.20	793.59
860.03	918.96	921.55
935.91	970.91	997.15
1018.11	1057.77	1112.97
1134.71	1193.90	1219.09
1308.43	1349.45	1370.18
1450.96	1495.01	1544.94
1634.06	1661.24	1669.95
2220.71	3182.84	3186.62
3191.83	3202.94	3210.10
3216.05	3272.81	3494.03

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.28 Vibration Frequencies [a,b] (cm^{-1}) for CDCD2

107.94	153.72	248.81
311.65	379.38	501.84
528.58	636.26	767.16
785.42	798.50	922.72
932.45	945.36	954.86
1034.44	1042.42	1069.06
1099.39	1303.98	1341.85
1349.38	1440.40	1476.93
1488.10	1666.64	1708.66
1719.57	3155.14	3156.34
3166.82	3170.04	3174.85
3245.33	3251.47	3254.84

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.29 Vibration Frequencies [a,b] (cm^{-1}) for CDCDCT

151.47	161.56	276.12
307.47	468.20	506.51
584.43	613.04	631.38
724.39	759.63	777.27
918.76	945.62	954.20
1027.97	1068.43	1330.65
1337.45	1435.81	1476.03
1655.68	1712.63	2226.05
3165.26	3177.98	3179.00
3259.40	3269.04	3494.90

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

Table 2.30 Vibration Frequencies [a,b] (cm^{-1}) for CDCT2

137.35	235.02	249.02
359.63	488.32	584.79
584.94	590.82	630.43
632.71	685.93	737.33
762.09	927.50	961.66
1288.09	1439.56	1651.56
2226.68	2233.17	3188.28
3283.52	3494.41	3495.04

[a]Nonscaled. Frequencies are calculated at the B3LYP/6-31G(d) level of theory.
[b]Torsion frequencies are not included in the calculation of Entropies S^{o}_{298} and Heat Capacities $C_p(T)$.

2.4.2 Enthalpies of Formation ($\Delta H_f^{o}{}_{298}$)

Enthalpies of formation ($\Delta H_f^{o}{}_{298}$) are estimated using total energies and calculated $\Delta H^{o}_{rxn,298}$ for the listed reactions(Table 2.32). Calculated $\Delta H^{o}_{rxn,298}$ for each reaction and evaluated literature thermodynamic properties for these reference reactants and products are utilized to estimate $\Delta H_f^{o}{}_{298}$ of the target species. Enthalpies of reaction ($\Delta H^{o}_{rxn,298}$) are estimated using total energies obtained by the density functional calculations. Zero-point energies (ZPVE's) and thermal correction to 298.15 K are taken into account. The total energies at 298 K from B3LYP/6-31G(d) calculation level, ZPVE's, and thermal corrections to 298.15 K are listed in Table 2.31.

Table 2.31 Total Energies at 298 K

Formula	Species	Molecular Weight	ZPVE[b]	Therm. Corr.[c]	Electronic Energy[d]	B3LYP /6-31G(d)[a]
C13H12	CCB2H2	168	0.210357	0.221618	-502.615372	-502.187604
C9H10	CCBCDH2	118	0.162145	0.17121	-348.956969	-348.626857
C8H8O	CCBCO	120	0.138079	0.146927	-384.879569	-384.597325
C9H8	CCBCT	116	0.137694	0.145687	-347.700884	-347.420257
C7H12	CCD2H2	68	0.113897	0.120847	-195.297772	-195.065306
C4H6O	CCDCO	70	0.089788	0.096552	-231.219843	-231.035299
C3H4O2	CCO2H2	72	0.065284	0.071919	-267.139597	-267.0037
C5H4	CCT2H2	68	0.06532	0.071867	-192.782876	-192.646995
C4H4O	CCTCO	64	0.065265	0.071863	-229.963583	-229.82776
C14H12	CDCB2	180	0.215327	0.227283	-540.702694	-540.264391
C10H10	CDCBCD	130	0.167325	0.177011	-387.045971	-386.704982
C10H8	CDCBCT	128	0.142837	0.152408	-385.79032	-385.497932
C6H8	CDCD2	80	0.119126	0.126657	-233.387827	-233.144427
C6H6	CDCDCT	78	0.094763	0.102116	-232.135083	-231.940099
C6H4	CDCT2	76	0.070322	0.077552	-230.873763	-230.727295

[a] Total Energy. Calculation based on the geometries optimized at B3LYP/6-31G(d) level of theory, ZPVE's and thermal corrections to 298 K are included. Units in Hartree.

[b] ZPVE: scaled zero-point energies in hartrees. Two hindered rotational frequencies are included in ZPVE which are scaled by 0.9806 (Scott[25] and Radom).

[c] Therm.Corr.: Thermal corrections in hartrees.

[d] B3LYP/6-31G(d) Electronic Energy (without considering ZPVE or Thermal Correction) Unit is Hartrees.

As an example, one reaction used to calculated $\Delta H_f^\circ{}_{298}$ CCBCDH2 is:

C9H10(CCBCDH2) + C2H4 = C7H8 + C4H6

$$\Delta H^\circ_{rxn,298} = \Delta H_f^\circ{}_{298}(C7H8) + \Delta H_f^\circ{}_{298}(C4H6) - \Delta H_f^\circ{}_{298}(C2H4) - \Delta H_f^\circ{}_{298}(CCBCDH2)$$

The reaction enthalpies and $\Delta H_f^\circ{}_{298}$'s of the species obtained from use of the reaction schemes are tabulated in Tables 2.32. Enthalpies of formation and uncertainties of reference species (data from literature) which are used to determine $\Delta H_f^\circ{}_{298}$ values of species studied in this work are listed in Table 2.33.

Isodesmic reaction used for Enthalpy calculation of each species is shown in Table 2.32.

$\Delta H_f^\circ{}_{298}$ of CCD2H2 is calculated as:

$$\Delta H^\circ_{rxn,298} = E_{298}(C3H6) + E_{298}(C4H6) - E_{298}(CCD2H2) - E_{298}(C2H4)$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(CCD2H2) = \Delta H_f^\circ{}_{298}(C3H6) + \Delta H_f^\circ{}_{298}(C4H6) - \Delta H_f^\circ{}_{298}(C2H4) - \Delta H^\circ_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCD2H2).

$\Delta H_f^\circ{}_{298}(CCD2H2)$ is calculated in this work to be 27.08 kcal/mol which is in reasonable agreement with the literature[41] reported value of 25.41 kcal/mol.

$\Delta H_f^\circ{}_{298}$ of CCB2H2 is calculated as:

$$\Delta H^\circ_{rxn,298} = E_{298}(C7H8) + E_{298}(C8H8) - E_{298}(CCB2H2) - E_{298}(C2H4)$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(CCB2H2) = \Delta H_f^\circ{}_{298}(C7H8) + \Delta H_f^\circ{}_{298}(C8H8) - \Delta H_f^\circ{}_{298}(C2H4) - \Delta H^\circ_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCB2H2).

$\Delta H_f^\circ{}_{298}(CCB2H2)$ is calculated in this work to be 42.41 kcal/mol which is in reasonable agreement with the literature[44] reported value of 39.39 kcal/mol.

$\Delta H_f^\circ{}_{298}$ of CCDCT is calculated as:

$$\Delta H^\circ_{rxn,298} = E_{298}(C3H4) + E_{298}(C4H6) - E_{298}(CCDCT) - E_{298}(C2H4)$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(CCDCT) = \Delta H_f^\circ{}_{298}(C3H4) + \Delta H_f^\circ{}_{298}(C4H6) - \Delta H_f^\circ{}_{298}(C2H4) - \Delta H^\circ_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCDCT).

$\Delta H_f^\circ{}_{298}$(CCDCT) is calculated in this work to be 67.62 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

$\Delta H_f^\circ{}_{298}$ of CCBCDH2 is calculated as:

$$\Delta H^\circ_{rxn,298} = E_{298}(C7H8) + E_{298}(C4H6) - E_{298}(CCBCDH2) - E_{298}(C2H4)$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(CCBCDH2) = \Delta H_f^\circ{}_{298}(C7H8) + \Delta H_f^\circ{}_{298}(C4H6) - \Delta H_f^\circ{}_{298}(C2H4) - \Delta H^\circ_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCBCDH2).

$\Delta H_f^\circ{}_{298}$(CCBCDH2) is calculated in this work to be 34.71 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

$\Delta H_f^\circ{}_{298}$ of CCT2H2 is calculated as:

$$\Delta H^\circ_{rxn,298} = E_{298}(C4H4) + E_{298}(C3H4) - E_{298}(CCT2H2) - E_{298}(C2H4)$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(CCT2H2) = \Delta H_f^\circ{}_{298}(C4H4) + \Delta H_f^\circ{}_{298}(C3H4) - \Delta H_f^\circ{}_{298}(C2H4) - \Delta H^\circ_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCT2H2).

$\Delta H_f^\circ{}_{298}$(CCT2H2) is calculated in this work to be 112.43 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

$\Delta H_f^\circ{}_{298}$ of CCBCT is calculated as:

$$\Delta H^\circ_{rxn,298} = E_{298}(C3H4) + E_{298}(C8H8) - E_{298}(CCBCT) - E_{298}(C2H4)$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(\text{CCBCT}) = \Delta H_f^\circ{}_{298}(\text{C3H4}) + \Delta H_f^\circ{}_{298}(\text{C8H8}) - \Delta H_f^\circ{}_{298}(\text{C2H4}) - \Delta H^\circ{}_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCBCT).

$\Delta H_f^\circ{}_{298}$(CCBCT) is calculated in this work to be 74.06 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

$\Delta H_f^\circ{}_{298}$ of CCO2H2 is calculated as:

$$\Delta H^\circ{}_{rxn,298} = E_{298}(\text{C2H4O}) + E_{298}(\text{C3H4O}) - E_{298}(\text{CCO2H2}) - E_{298}(\text{C2H4})$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(\text{CCO2H2}) = \Delta H_f^\circ{}_{298}(\text{C2H4O}) + \Delta H_f^\circ{}_{298}(\text{C3H4O}) - \Delta H_f^\circ{}_{298}(\text{C2H4}) - \Delta H^\circ{}_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCO2H2).

$\Delta H_f^\circ{}_{298}$(CCO2H2) is calculated in this work to be -64.88 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

$\Delta H_f^\circ{}_{298}$ of CDCD2 is calculated as:

$$\Delta H^\circ{}_{rxn,298} = E_{298}(\text{C4H6}) + E_{298}(\text{C4H6}) - E_{298}(\text{CDCD2}) - E_{298}(\text{C2H4})$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(\text{CDCD2}) = \Delta H_f^\circ{}_{298}(\text{C4H6}) + \Delta H_f^\circ{}_{298}(\text{C4H6}) - \Delta H_f^\circ{}_{298}(\text{C2H4}) - \Delta H^\circ{}_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CDCD2).

$\Delta H_f^\circ{}_{298}$(CDCD2) is calculated in this work to be 44.54 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

$\Delta H_f^\circ{}_{298}$ of CDCDCT is calculated as:

$$\Delta H^\circ_{rxn,298} = E_{298}(C4H4) + E_{298}(C4H6) - E_{298}(CDCDCT) - E_{298}(C2H4)$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(CDCDCT) = \Delta H_f^\circ{}_{298}(C4H4) + \Delta H_f^\circ{}_{298}(C4H6) - \Delta H_f^\circ{}_{298}(C2H4) - \Delta H^\circ_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CDCDCT).

$\Delta H_f^\circ{}_{298}(CDCDCT)$ is calculated in this work to be 85.45 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

$\Delta H_f^\circ{}_{298}$ of CDCBCT is calculated as:

$$\Delta H^\circ_{rxn,298} = E_{298}(C8H8) + E_{298}(C4H4) - E_{298}(CDCBCT) - E_{298}(C2H4)$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(CDCBCT) = \Delta H_f^\circ{}_{298}(C8H8) + \Delta H_f^\circ{}_{298}(C4H4) - \Delta H_f^\circ{}_{298}(C2H4) - \Delta H^\circ_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CDCBCT).

$\Delta H_f^\circ{}_{298}(CDCBCT)$ is calculated in this work to be 94.96 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

$\Delta H_f^\circ{}_{298}$ of CCDCO is calculated as:

$$\Delta H^\circ_{rxn,298} = E_{298}(C3H6) + E_{298}(C3H4O) - E_{298}(CCDCO) - E_{298}(C2H4)$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(CCDCO) = \Delta H_f^\circ{}_{298}(C3H6) + \Delta H_f^\circ{}_{298}(C3H4O) - \Delta H_f^\circ{}_{298}(C2H4) - \Delta H^\circ_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCDCO).

$\Delta H_f^\circ{}_{298}$(CCDCO) is calculated in this work to be -20.68 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

$\Delta H_f^\circ{}_{298}$ of CCTCO is calculated as:

$$\Delta H^\circ_{rxn,298} = E_{298}(C3H4) + E_{298}(C3H4O) - E_{298}(CCTCO) - E_{298}(C2H4)$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(CCTCO) = \Delta H_f^\circ{}_{298}(C3H4) + \Delta H_f^\circ{}_{298}(C3H4O) - \Delta H_f^\circ{}_{298}(C2H4) - \Delta H^\circ_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCTCO).

$\Delta H_f^\circ{}_{298}$(CCTCO) is calculated in this work to be 19.72 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

$\Delta H_f^\circ{}_{298}$ of CCBCO is calculated as:

$$\Delta H^\circ_{rxn,298} = E_{298}(C7H8) + E_{298}(C3H4O) - E_{298}(CCBCO) - E_{298}(C2H4)$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(CCBCO) = \Delta H_f^\circ{}_{298}(C7H8) + \Delta H_f^\circ{}_{298}(C3H4O) - \Delta H_f^\circ{}_{298}(C2H4) - \Delta H^\circ_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CCBCO).

$\Delta H_f^\circ{}_{298}$(CCBCO) is calculated in this work to be -13.35 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

$\Delta H_f^\circ{}_{298}$ of CDCBCD is calculated as:

$$\Delta H^\circ_{rxn,298} = E_{298}(C4H4) + E_{298}(C4H4) - E_{298}(CDCBCD) - E_{298}(C2H4)$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(\text{CDCBCD}) = \Delta H_f^\circ{}_{298}(\text{C4H4}) + \Delta H_f^\circ{}_{298}(\text{C4H4}) - \Delta H_f^\circ{}_{298}(\text{C2H4}) - \Delta H^\circ{}_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CDCBCD).

$\Delta H_f^\circ{}_{298}$(CDCBCD) is calculated in this work to be 52.34 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

$\Delta H_f^\circ{}_{298}$ of CDCT2 is calculated as:

$$\Delta H^\circ{}_{rxn,298} = E_{298}(\text{C4H4}) + E_{298}(\text{C4H4}) - E_{298}(\text{CDCT2}) - E_{298}(\text{C2H4})$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(\text{CDCT2}) = \Delta H_f^\circ{}_{298}(\text{C4H4}) + \Delta H_f^\circ{}_{298}(\text{C4H4}) - \Delta H_f^\circ{}_{298}(\text{C2H4}) - \Delta H^\circ{}_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CDCT2).

$\Delta H_f^\circ{}_{298}$(CDCT2) is calculated in this work to be 131.68 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

$\Delta H_f^\circ{}_{298}$ of CDCB2 is calculated as:

$$\Delta H^\circ{}_{rxn,298} = E_{298}(\text{C8H8}) + E_{298}(\text{C8H8}) - E_{298}(\text{CDCB2}) - E_{298}(\text{C2H4})$$

where E_{298} is the B3LYP/6-31G(d) Energy (ZPVE's and thermal corrections to 298 K are included)

$$\Delta H_f^\circ{}_{298}(\text{CDCB2}) = \Delta H_f^\circ{}_{298}(\text{C8H8}) + \Delta H_f^\circ{}_{298}(\text{C8H8}) - \Delta H_f^\circ{}_{298}(\text{C2H4}) - \Delta H^\circ{}_{rxn,298}$$

where $\Delta H_f^\circ{}_{298}$ is the Enthalpy of formation of species, known for three species in the reaction, and calculated for the fourth species (CDCB2).

$\Delta H_f^\circ{}_{298}$(CDCB2) is calculated in this work to be 60.86 kcal/mol. No $\Delta H_f^\circ{}_{298}$ value for this species were found in the literature.[11,12,13,14,15]

Table 2.32 Calculated Enthalpies at 298K

Reaction						$\Delta H_{rxn}^{o}{}_{298}$ [a]	$\Delta H_{f}^{o}{}_{298}$ [a]
C5H8(CCD2H2)	+	C2H4	--->	C3H6	+ C4H6	-8.74	27.08
C13H12(CCB2H2)	+	C2H4	--->	C7H8	+ C8H8	-7.87	42.39
C5H6(CCDCT)	+	C2H4	--->	C3H4	+ C4H6	-9.84	67.62
C9H10(CCBCDH2)	+	C2H4	--->	C7H8	+ C4H6	-9.29	34.71
C5H4(CCT2H2)	+	C2H4	--->	C4H4	+ C3H4	-10.15	112.43
C9H8(CCBCT)	+	C2H4	--->	C8H8	+ C3H4	-7.18	74.06
C3H4O2(CCO2H2)	+	C2H4	--->	C2H4O	+ C3H4O	-8.54	-64.88
C6H8(CDCD2)	+	C2H4	--->	C4H6	+ C4H6	-5.07	44.54
C6H6(CDCDCT)	+	C2H4	--->	C4H6	+ C4H4	-1.48	85.45
C10H8(CDCBCT)	+	C2H4	--->	C8H8	+ C4H4	-1.88	94.96
C4H6O(CCDCO)	+	C2H4	--->	C3H6	+ C3H4O	-7.06	-20.68
C4H4O(CCTCO)	+	C2H4	--->	C3H4	+ C3H4O	-8.03	19.72
C8H8O(CCBCO)	+	C2H4	--->	C7H8	+ C3H4O	-7.32	-13.35
C10H10(CDCBCD)	+	C2H4	--->	C4H6	+ C8H8	-3.77	52.34
C6H4(CDCT2)	+	C2H4	--->	C4H4	+ C4H4	-3.20	131.68
C14H12(CDCB2)	+	C2H4	--->	C8H8	+ C8H8	-3.18	60.86

[a] Reaction enthalpies obtained at B3LYP/6-31G(d). Reaction enthalpies include thermal correction and zero-point energy. Units in kcal/mol. Reactions are isodesmic. No reaction series conserves groups. Uncertainties of reference compound enthalpy not included. Species Enthalpy Values are for the lowest energy conformer and corrections have not been made for higher energy conformers.

Table 2.33 Total Energies at 298 K and $\Delta H_{f}^{o}{}_{298}$ for Reference Species in the Reaction Schemes

Name	Formula	B3LYP /6-31G(d) [a]	ZPVE [b]	Therm. Corr. [c]	$\Delta H_{f}^{o}{}_{298}$ [d]
Ethylene	C2H4	-78.482054	0.05122	0.055207	12.54[e]
Propylene	C3H6	-117.744	0.080067	0.085085	4.87[f]
Acetaldehyde	C2H4O	-153.71475	0.055824	0.060661	-40.8[g] ± 0.35
Acrolein	C3H4O	-191.7846	0.061652	0.066951	-20.08[h]
Vinylacetylene	C4H4	-154.60723	0.061176	0.066619	70.51[i]
Propyne	C3H4	-116.538	0.055721	0.060661	44.31[j] ± 0.21
Styrene	C8H8	-309.37576	0.133732	0.141446	35.11[k] ± 0.24
Toluene	C7H8	-271.30644	0.128231	0.134519	11.95[l] ± 0.15
1,3-Butadiene	C4H6	-155.81728	0.085492	0.091081	26.00[m] ± 0.19

[a] Total Energy. Calculation based on the geometries optimized at B3LYP/6-31G(d) level of theory, ZPVE's and thermal corrections to 298 K are included. Units in Hartree.

[b] ZPVE: scaled zero-point energies in hartrees. Two hindered rotational frequencies are included in ZPVE which are scaled by 0.9806 (Scott and Radom).

[c] Therm.Corr.: Thermal corrections in hartrees.

[d] Units in kcal/mol.

The uncertainties are given in the reference.
[e] Reference 34 [f] Reference 35 [g] Reference 36 [h] Reference 11
[I] Reference 37 [j] Reference 38 [k] Reference 39 [l] Reference 39
[m] Reference 40

The accuracy of the enthalpies of formation obtained theoretically is controlled by several factors: the level of sophistication (method + basis set) applied to calculate the electronic energy, the reliability of the enthalpies of formation of the reference compounds, the uncertainty in the thermal corrections, and the choice of the working chemical reaction used in the cancellation of calculation errors. The ZPVE and thermal correction in data of Table 2.31 have small contributions to the error on relative base. Scott[25] and Radom report errors after scaling (0.9806) for B3LYP/6-31G(d,p) of 0.1 kcal/mol for ZPVE in their study on 39 molecules incorporating 1066 known vibrations. They also report errors of 0.01 kcal/mol for thermal correction from 0 to 298 K in density function theory.[25] These reported error values are likely smaller than in this study; but in this work it has been assumed that the errors are non-random and that they are cancelled in the isodesmic reactions to a significant extent.

2.4.3 Rotational Barriers

Potential barriers for internal rotations of C-C bonds in the species are calculated at the B3LYP/3-21G, B3LYP/6-31G(d), B3LYP/6-31G(d,p) and in some cases at the B3LYP/6-31+g(d,p) levels of theory (please refer to the Figures 2.16 to 2.37 for details). Potential energy as function of dihedral angle is determined by scanning the torsion angles from 0° to 360° at 15° intervals and allowing the remaining molecular structural

parameters to be optimized – relaxed scan. Some molecules have the internal rotation potentials calculated using a rigid scan method as noted in the Figures 2.17 to 2.37, on a case-by-case basis.

Rotation data for the C–C bonds in the species are shown in Table 2.34, which indicates the rotational barriers and the foldness obtained from the rotations. The geometries at the points of these minima are optimized at the B3LYP/6-31G(d) level. The barriers for internal rotations are calculated from the differences between the total energy of each structure and that of the global equilibrium. The total energies and calculated rotation barriers about C–C bond for each rotational structure of the species listed in Tables 2.35 to 2.47. Potential Energy vs. Torsion angle diagrams for internal rotations about C–C bond of the species are shown in Figures 2.16 to 2.37. Points are values calculated using relaxed and non-relaxed density functional B3LYP calculations.

Table 2.34 Moments of Inertia of Rotors, Rotational Barrier and Foldness

Species		MI-1[a]	MI-2[b]	V[c]	n[d]
CCB2H2					
	C6H5-CH2C6H5	89	161.15	0.62	4
	C6H5-CH2C6H5	89	161.15	1.84	2
CCBCDH2					
	C6H5-CH2C2H3	89	58.6	2.27	2
	C2H3-CH2C6H5	19.73	161.15	3.83	3
CCBCOH2					
	C6H5-CH2CHO	89	62.78	6.7	2
	CHO-CH2C6H5	18.74	161.15	2.23	2
CCBCTH2					
	C6H5-CH2C2H	89	54.41	0.39	2
CCD2H2					
	CH2(C2H3)-C2H3	58.6	19.73	2.47	2
	CH2(C2H3)-C2H3	58.6	19.73	1.79	2
CCDCOH2					
	CHO-CH2C2H3	18.74	58.6	2.32	3
	C2H3-CH2CHO	19.73	62.78	2.63	3
CCO2H2					
	CHO-CH2CHO	18.74	62.78	0.66	4
	CHO-CH2CHO	18.74	62.78	0.54	4
CCOCTH2					
	CHO-CH2C2H	18.74	54.41	2.65	2
CDCB2					
	C6H5-C(CH2)C6H	89	154.04	2.57	4
	C6H5-C(CH2)C6H	89	154.04	9.37	2
CDCBCD					
	C6H5-C(CH2)C2H3	89	66.26	2.69	4
CDCBCT					
	C6H5-C(CH2)C2H	89	62.75	2.97	2
CDCD2					
	C2H3-C(CH2)C2H	19.73	66.26	4.99	2
	C2H3-C(CH2)C2H	19.73	66.26	5.71	4
CDCDCT					
	C2H3-C(CH2)C2H	19.73	62.75	5.76	2

[a] Moment of Inertia of the group on left of rotor (as represented here), Units in amu-Bohr^2

[b] Moment of Inertia of the group on right of rotor (as represented here), Units in amu-Bohr^2

[c] Rotation Barrier, Units in kcal

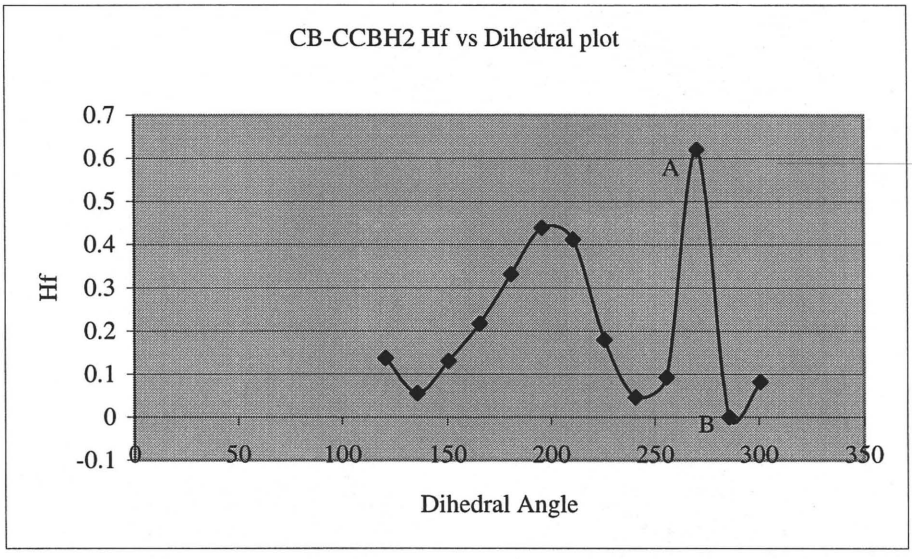
[d] Foldness from Rotation Plot shown in Figures 2.16 to 2.37

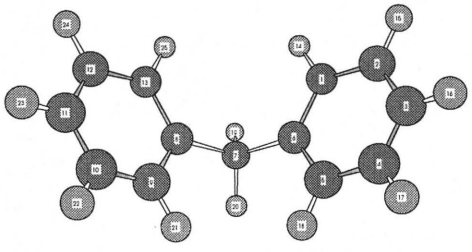
Table 2.35 Total Energy and Internal Rotation Barriers for CCB2H2

CB-CCBH2			CB-CCBH2		
Torsion Angle	Total Energy [a]	Rotational barrier[b]	Torsion Angle	Total Energy [a]	Rotational barrier[b]
120.71	-499.859379	0.14	89.70	-499.858547	0.55
135.71	-499.859509	0.06	134.70	-499.859419	0.00
150.71	-499.859391	0.13	179.70	-499.858806	0.38
165.71	-499.859253	0.22	224.70	-499.856487	1.84
180.71	-499.859069	0.33	269.70	-499.858597	0.52
195.71	-499.858898	0.44			
210.71	-499.858941	0.41			
225.71	-499.859312	0.18			
240.71	-499.859524	0.05			
255.71	-499.85945	0.09			
270.71	-499.85861	0.62			
285.71	-499.859598	0.00			
300.71	-499.859467	0.08			

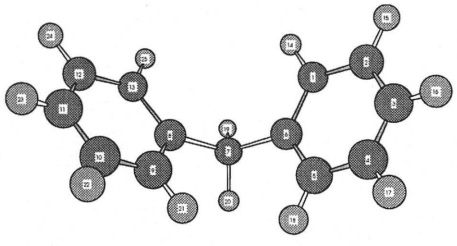
[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

[b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.



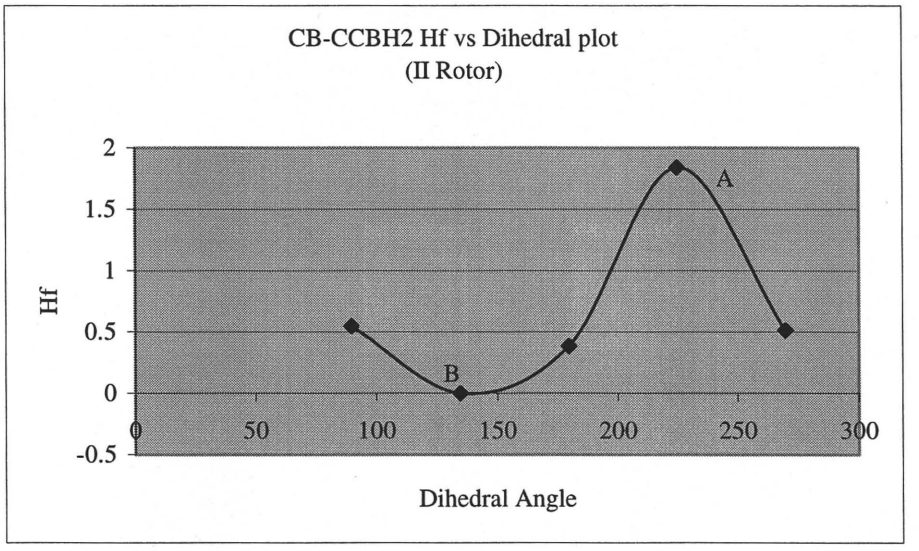


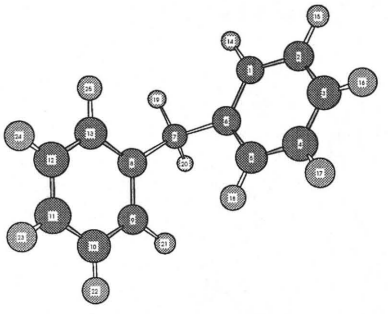
Structure at point A



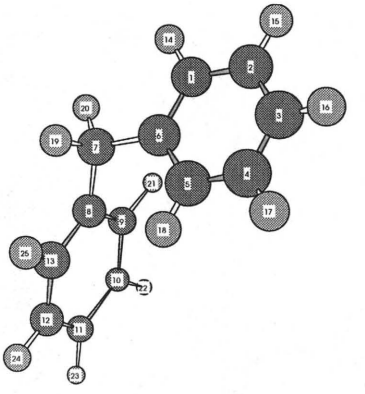
Structure at point B

Figure 2.16 Potential Barriers for Internal Rotation about CB-CCBH2 bond (Dihedral 9-8-7-6) of CCB2H2. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.35 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*





Structure at point A



Structure at point B

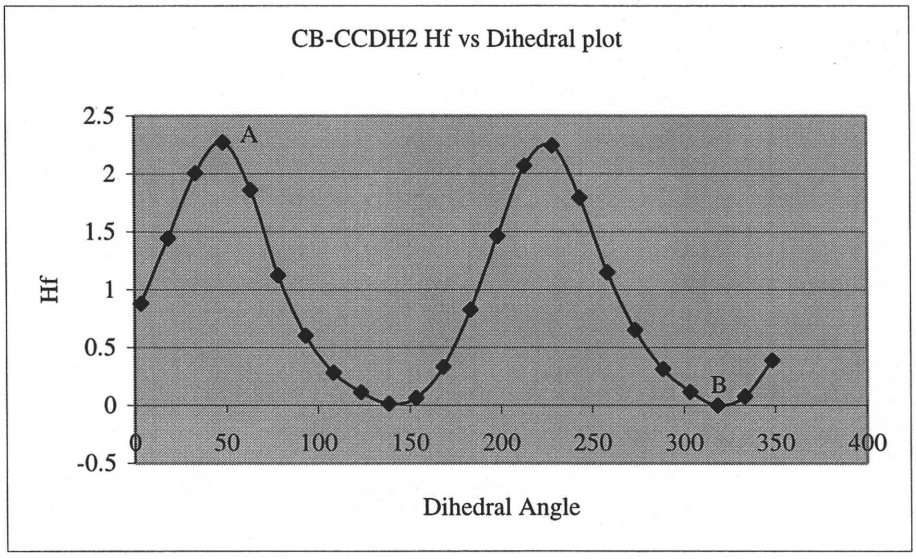
Figure 2.17 Potential Barriers for Internal Rotation about CB-CCBH2 bond (Dihedral 8-7-6-1) of CCB2H2. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.35 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

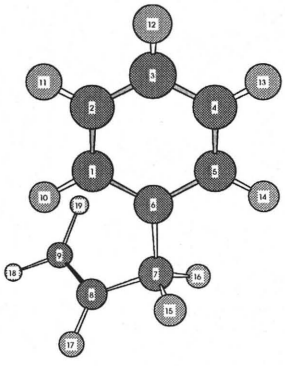
Table 2.36 Total Energy and Internal Rotation Barriers for CCBCDH2

CB-CCDH2			CD-CCBH2		
Torsion Angle	Total Energy [a]	Rotational barrier[b]	Torsion Angle	Total Energy [a]	Rotational barrier[b]
3.35	-347.046208	0.88	7.67	-347.045797	1.05
18.35	-347.04531	1.44	22.67	-347.044465	1.88
33.35	-347.044415	2.01	37.67	-347.043223	2.66
48.35	-347.043992	2.27	52.67	-347.04286	2.89
63.35	-347.044647	1.86	67.67	-347.043896	2.24
78.35	-347.045817	1.13	82.67	-347.045796	1.05
93.35	-347.046651	0.60	97.67	-347.047326	0.09
108.35	-347.047157	0.28	112.67	-347.047398	0.04
123.35	-347.047431	0.11	127.67	-347.046586	0.55
138.35	-347.047587	0.01	142.67	-347.045253	1.39
153.35	-347.047507	0.07	157.67	-347.044057	2.14
168.35	-347.047081	0.33	172.67	-347.043968	2.19
183.35	-347.046292	0.83	187.67	-347.045226	1.40
198.35	-347.045278	1.46	202.67	-347.046657	0.51
213.35	-347.044315	2.07	217.67	-347.047462	0.00
228.35	-347.044034	2.24	232.67	-347.04736	0.06
243.35	-347.04475	1.80	247.67	-347.046171	0.81
258.35	-347.045779	1.15	262.67	-347.043838	2.27
273.35	-347.046572	0.65	277.67	-347.041351	3.83
288.35	-347.047109	0.31	292.67	-347.042587	3.06
303.35	-347.047426	0.12	307.67	-347.044537	1.84
318.35	-347.047611	0.00	322.67	-347.045893	0.98
333.35	-347.047485	0.08	337.67	-347.046647	0.51
348.35	-347.046992	0.39	352.67	-347.046609	0.54

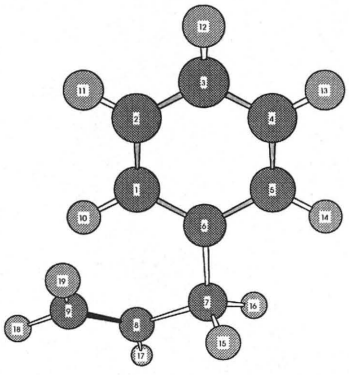
[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

[b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.



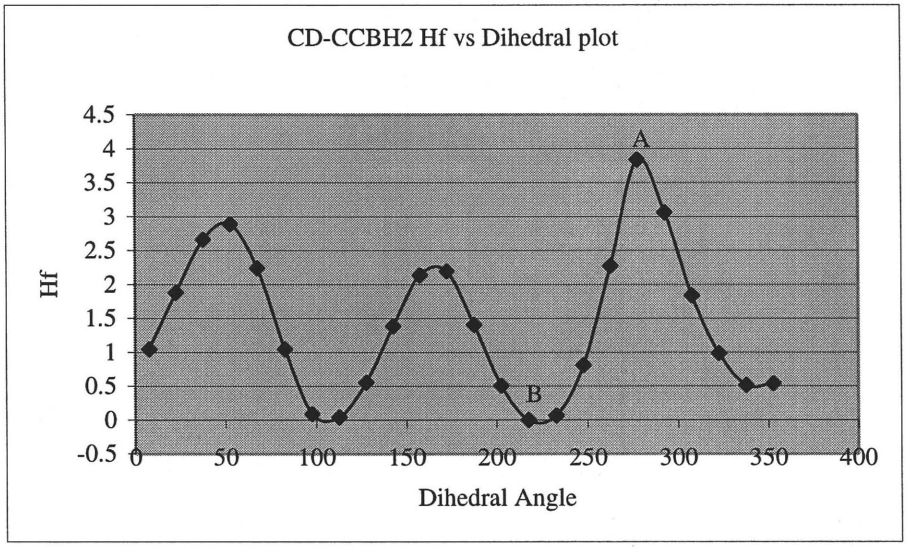


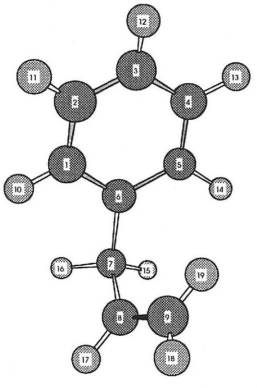
Structure at point A



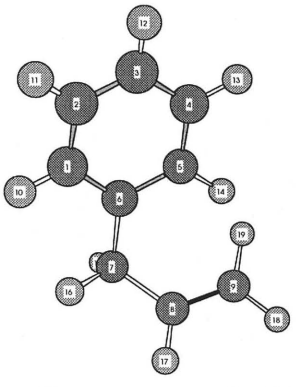
Structure at point B

Figure 2.19 Potential Barriers for Internal Rotation about CB-CCDH2 bond (Dihedral 9-8-7-6) of CCBCDH2. Points are Calculated Values at B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.36 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*





Structure at point A



Structure at point B

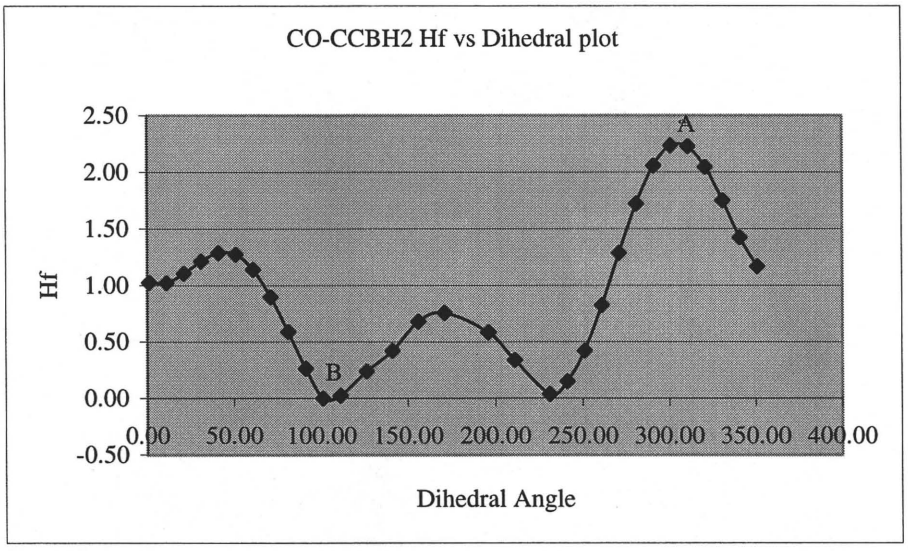
Figure 2.18 Potential Barriers for Internal Rotation about CD-CCBH2 bond (Dihedral 8-7-6-1) of CCBCDH2. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.36 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

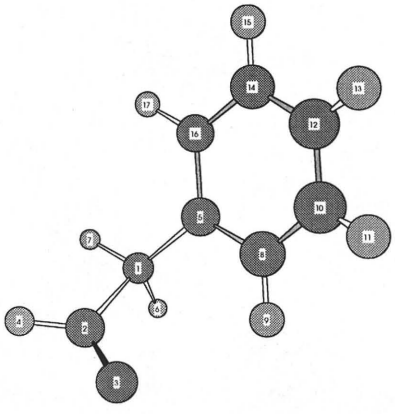
Table 2.37 Total Energy and Internal Rotation Barriers for CCBCOH2

CO-CCBH2			CB-CCOH2		
Torsion Angle	Total Energy [a]	Rotational barrier[b]	Torsion Angle	Total Energy [a]	Rotational barrier[b]
1.14	-384.887657	1.03	101.58	-384.889172	0.10
11.14	-384.887665	1.02	111.58	-384.888833	0.31
21.14	-384.887534	1.10	121.58	-384.887992	0.84
31.14	-384.887361	1.21	131.58	-384.886313	1.89
41.14	-384.887241	1.29	141.58	-384.883715	3.52
51.14	-384.887265	1.27	151.58	-384.880772	5.37
61.14	-384.887476	1.14	161.58	-384.87872	6.66
71.14	-384.887862	0.90	171.58	-384.878661	6.70
81.14	-384.888353	0.59	181.58	-384.880455	5.57
91.14	-384.888868	0.27	191.58	-384.883041	3.95
101.14	-384.889291	0.00	201.58	-384.885403	2.46
221.14	-384.889172	0.07	211.58	-384.887105	1.40
231.14	-384.889233	0.04	221.58	-384.88816	0.73
241.14	-384.889051	0.15	231.58	-384.88877	0.35
251.14	-384.888619	0.42	241.58	-384.889095	0.15
261.14	-384.887977	0.82	251.58	-384.889263	0.04
271.14	-384.887244	1.28	261.58	-384.889331	0.00
281.14	-384.886551	1.72	271.58	-384.889317	0.01
291.14	-384.886014	2.06	281.58	-384.88917	0.10
301.14	-384.88573	2.23	291.58	-384.888829	0.31
311.14	-384.885744	2.23	301.58	-384.887986	0.84
321.14	-384.886031	2.05	311.58	-384.886308	1.90
331.14	-384.886502	1.75	321.58	-384.883718	3.52
341.14	-384.887023	1.42	331.58	-384.880796	5.36
351.14	-384.887433	1.17	341.58	-384.878776	6.62

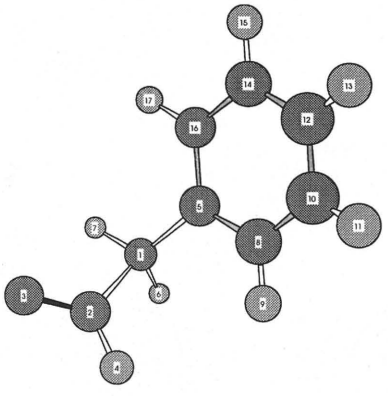
[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

[b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.



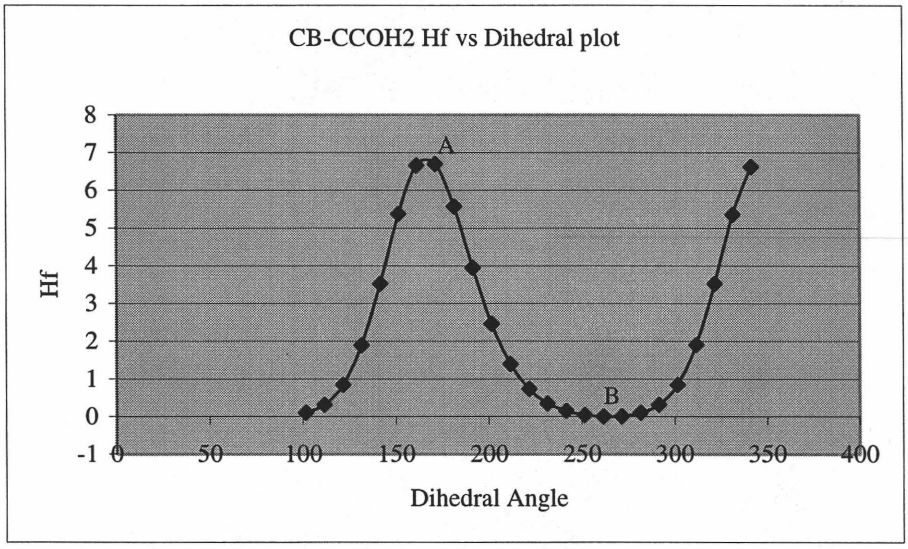


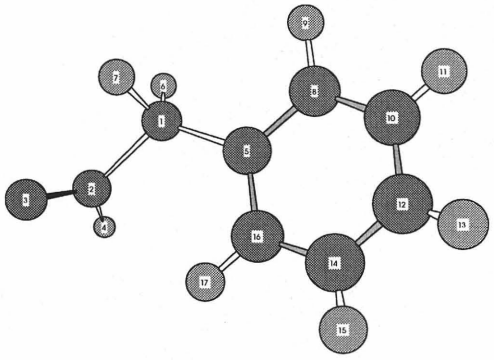
Structure at point A



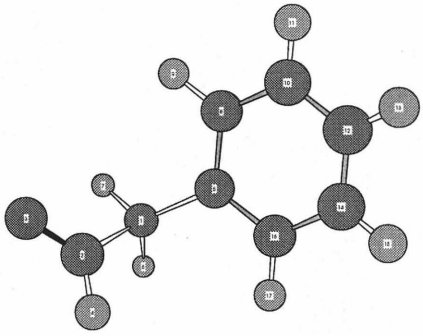
Structure at point B

Figure 2.20 Potential Barriers for Internal Rotation about CO-CCBH2 bond (Dihedral 5-1-2-3) of CCBCOH2. Points are Calculated Values at relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.37 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*. Energy Values between 101 degrees and 231 degrees have been estimated from the energy values for CO-CCDH2 plot. (Figure 2.25)





Structure at point A



Structure at point B

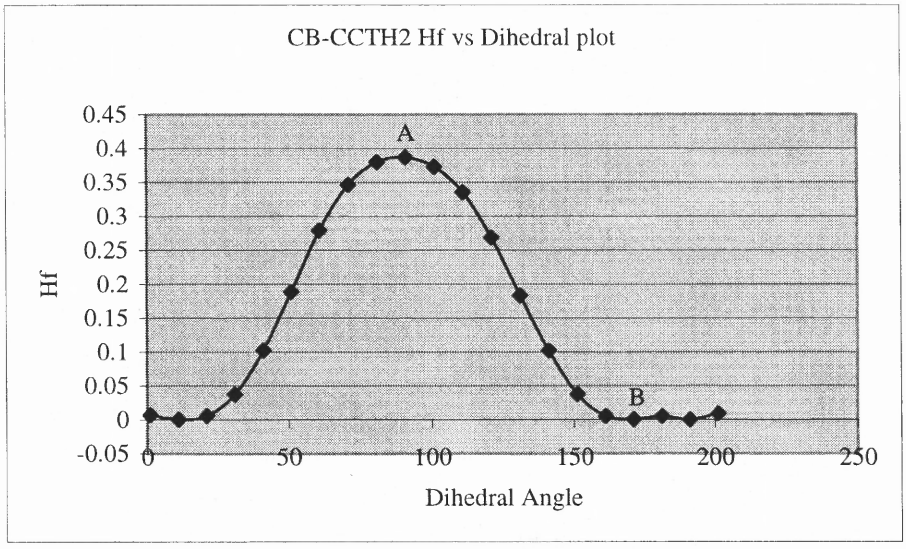
Figure 2.21 Potential Barriers for Internal Rotation about CB-CCOH2 bond (Dihedral 8-5-1-2) of CCBCOH2. Points are Calculated Values at relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.37 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

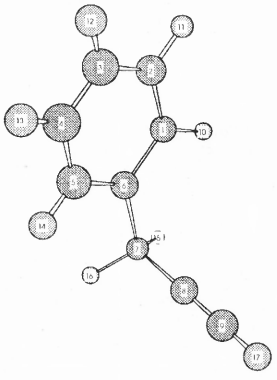
Table 2.38 Total Energy and Internal Rotation Barriers for CCBCTH2

	CB-CCTH2	
Torsion Angle	Total Energy [a]	Rotational barrier[b]
1.06	-347.700881	0.01
11.06	-347.700891	0.00
21.06	-347.700883	0.01
31.06	-347.700832	0.04
41.06	-347.700729	0.10
51.06	-347.700592	0.19
61.06	-347.700447	0.28
71.06	-347.70034	0.35
81.06	-347.700287	0.38
91.06	-347.700276	0.39
101.06	-347.700298	0.37
111.06	-347.700358	0.34
121.06	-347.700464	0.27
131.06	-347.7006	0.18
141.06	-347.70073	0.10
151.06	-347.700832	0.04
161.06	-347.700884	0.01
171.06	-347.700891	0.00
181.06	-347.700884	0.01
191.06	-347.700892	0.00
201.06	-347.700877	0.01

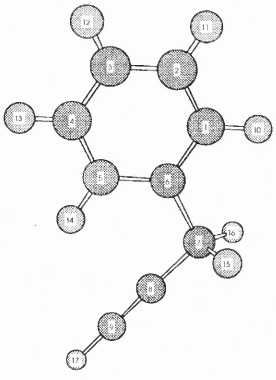
[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

[b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.





Structure at point A



Structure at point B

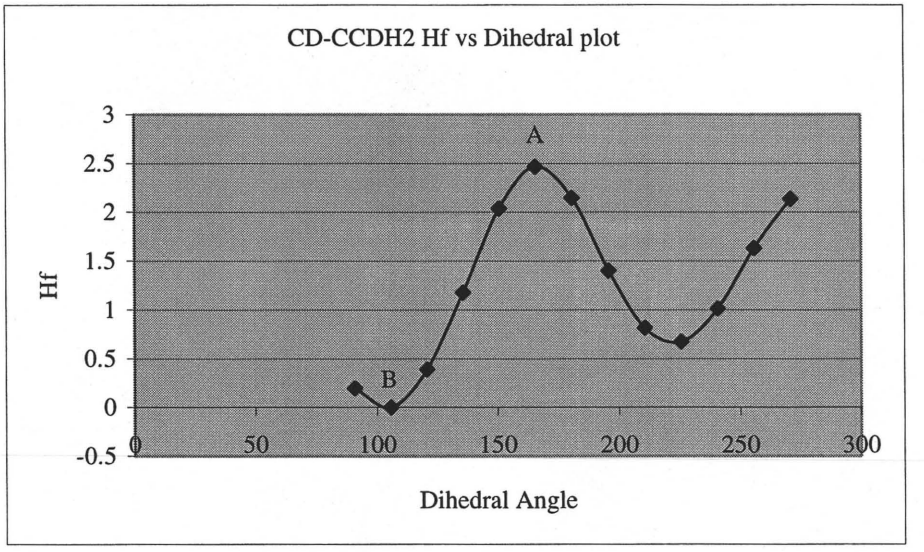
Figure 2.22 Potential Barriers for Internal Rotation about CB-CCTH2 bond (Dihedral 8-7-6-1) of CCBCTH2. Points are Calculated Values at non-relaxed B3LYP/6-31G(d) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.38 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

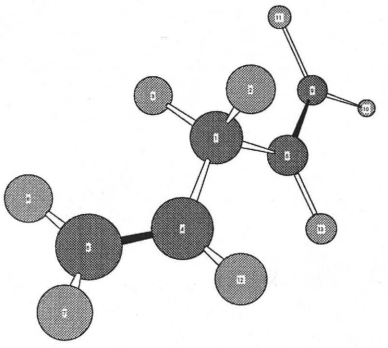
Table 2.39 Total Energy and Internal Rotation Barriers for CCD2H2

CD-CCDH2			CD-CCDH2		
Torsion Angle	Total Energy [a]	Rotational barrier[b]	Torsion Angle	Total Energy [a]	Rotational barrier[b]
90.74	-195.297358	0.20	60.74	-195.294227	1.49
105.74	-195.29767	0.00	75.74	-195.294277	1.46
120.74	-195.297048	0.39	90.74	-195.296141	0.29
135.74	-195.295794	1.18	105.74	-195.296602	0.00
150.74	-195.294425	2.04	120.74	-195.295313	0.81
165.74	-195.29374	2.47	135.74	-195.295313	0.81
180.74	-195.294248	2.15	150.74	-195.294205	1.50
195.74	-195.295439	1.40	165.74	-195.293749	1.79
210.74	-195.296373	0.81	180.74	-195.294483	1.33
225.74	-195.2966	0.67	195.74	-195.294557	1.28
240.74	-195.296056	1.01			
255.74	-195.295067	1.63			
270.74	-195.294267	2.14			
285.74	-195.294233	2.16			
300.74	-195.295118	1.60			
315.74	-195.296241	0.90			
330.74	-195.296764	0.57			
345.74	-195.296354	0.83			
360.74	-195.295234	1.53			

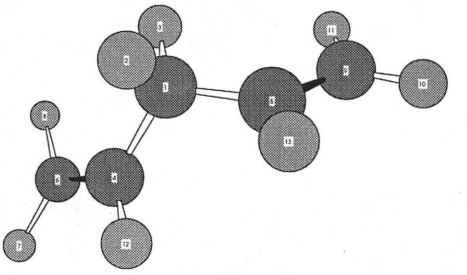
[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

[b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.



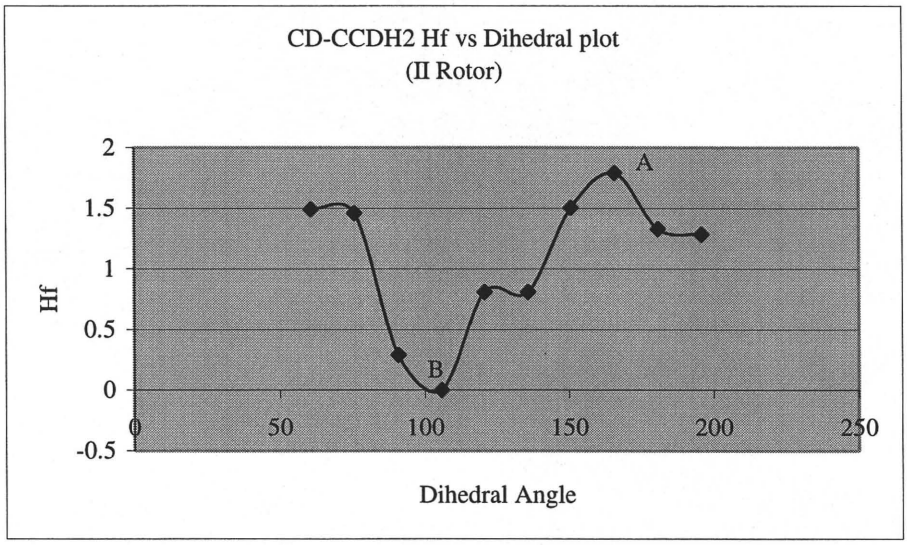


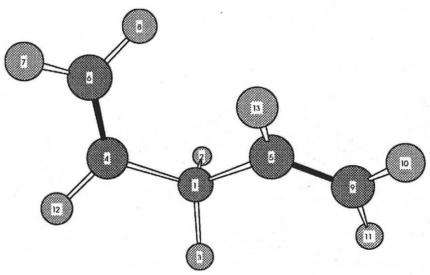
Structure at point A



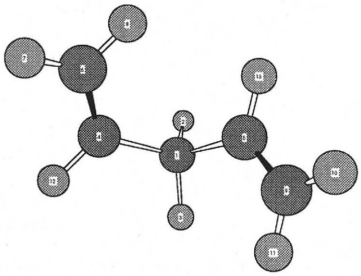
Structure at point B

Figure 2.23 Potential Barriers for Internal Rotation about CD-CCDH2 bond (Dihedral 9-5-1-4) of CCD2H2. Points are Calculated Values at non-relaxed B3LYP/6-31G(d) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.39 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*





Structure at point A



Structure at point B

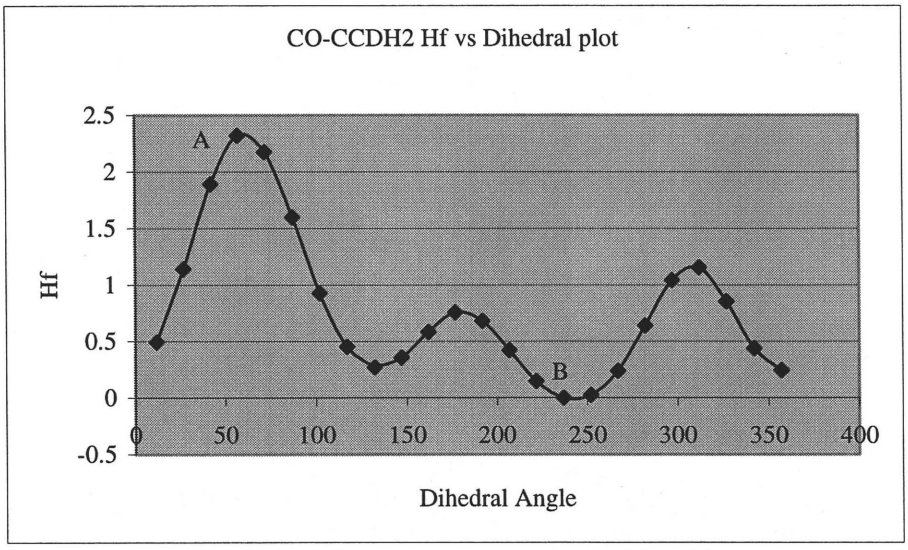
Figure 2.24 Potential Barriers for Internal Rotation about CD-CCDH2 bond (Dihedral 9-5-1-4) of CCD2H2. Points are Calculated Values at non-relaxed B3LYP/6-31G(d) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.39 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

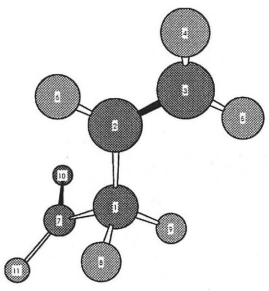
Table 2.40 Total Energy and Internal Rotation Barriers for CCDCOH2

CO-CCDH2			CD-CCOH2		
Torsion Angle	Total Energy [a]	Rotational barrier[b]	Torsion Angle	Total Energy [a]	Rotational barrier[b]
11.95	-231.241165	0.50	0.90	-231.238214	2.35
26.95	-231.240139	1.14	15.90	-231.238936	1.89
41.95	-231.23894	1.89	30.90	-231.240122	1.15
56.95	-231.238255	2.32	45.90	-231.241136	0.51
71.95	-231.23849	2.18	60.90	-231.241524	0.27
86.95	-231.23941	1.60	60.90	-231.241524	0.27
101.95	-231.240479	0.93	75.90	-231.241235	0.45
116.95	-231.241236	0.45	90.90	-231.240494	0.92
131.95	-231.241524	0.27	105.90	-231.239775	1.37
131.95	-231.241525	0.27	120.90	-231.23951	1.53
146.95	-231.241388	0.36	135.90	-231.239735	1.39
161.95	-231.241026	0.58	150.90	-231.240028	1.21
176.95	-231.240749	0.76	165.90	-231.239868	1.31
191.95	-231.240872	0.68	180.90	-231.23913	1.77
206.95	-231.241287	0.42	195.90	-231.238192	2.36
221.95	-231.241719	0.15	210.90	-231.237769	2.63
236.95	-231.241956	0.00	225.90	-231.238258	2.32
251.95	-231.241916	0.02	240.90	-231.239315	1.66
266.95	-231.241573	0.24	255.90	-231.24046	0.94
281.95	-231.240936	0.64	270.90	-231.24143	0.33
296.95	-231.240297	1.04	285.90	-231.241955	0.00
311.95	-231.240122	1.15	300.90	-231.24178	0.11
326.95	-231.240594	0.85	315.90	-231.240882	0.67
341.95	-231.241257	0.44	330.90	-231.239585	1.49
356.95	-231.241568	0.24	345.90	-231.238483	2.18

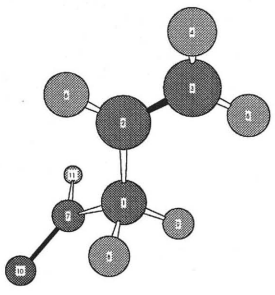
[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

[b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.



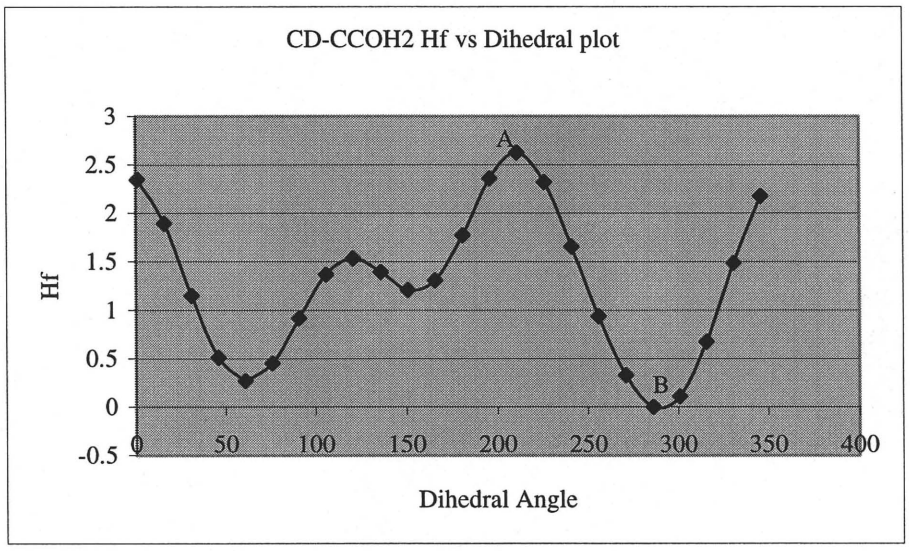


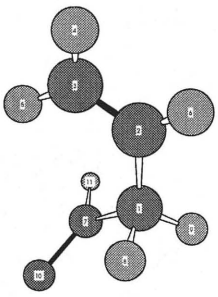
Structure at point A



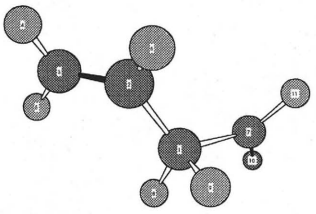
Structure at point B

Figure 2.25 Potential Barriers for Internal Rotation about CO-CCDH2 bond (Dihedral 10-7-1-2) of CCDCOH2. Points are Calculated Values at non-relaxed B3LYP/6-31+G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.40 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*





Structure at point A



Structure at point B

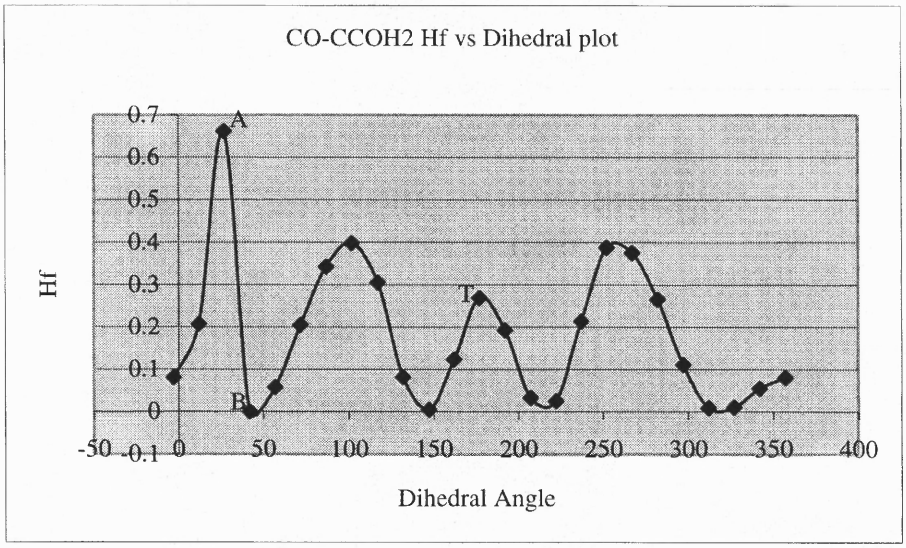
Figure 2.26 Potential Barriers for Internal Rotation about CD-CCOH2 bond (Dihedral 7-1-2-6) of CCDCOH2. Points are Calculated Values at non-relaxed B3LYP/6-31+G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.40 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

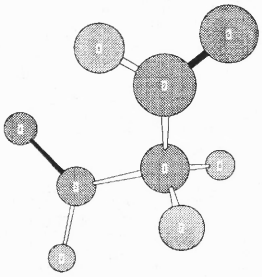
Table 2.41 Total Energy and Internal Rotation Barriers for CCO2H2

CO-CCOH2			CO-CCOH2		
Torsion Angle	Total Energy [a]	Rotational barrier[b]	Torsion Angle	Total Energy [a]	Rotational barrier[b]
12.02	-267.145021	0.21	9.05	-267.1451	0.16
27.02	-267.144297	0.66	24.05	-267.144489	0.54
42.02	-267.145351	0.00	39.05	-267.145349	0.00
57.02	-267.145259	0.06	54.05	-267.145285	0.04
72.02	-267.145024	0.21	69.05	-267.145075	0.17
87.02	-267.144805	0.34	84.05	-267.144847	0.31
102.02	-267.144717	0.40	99.05	-267.144724	0.39
117.02	-267.144865	0.31	114.05	-267.14481	0.34
132.02	-267.145221	0.08	129.05	-267.14516	0.12
147.02	-267.145344	0.00	144.05	-267.145347	0.00
162.02	-267.145155	0.12	144.05	-267.145348	0.00
177.02	-267.144923	0.27	159.05	-267.145215	0.08
192.02	-267.145044	0.19	174.05	-267.144953	0.25
207.02	-267.145299	0.03	189.05	-267.144995	0.22
222.02	-267.145311	0.02	204.05	-267.145266	0.05
237.02	-267.14501	0.21	219.05	-267.145335	0.01
252.02	-267.144734	0.39	234.05	-267.145088	0.16
267.02	-267.144754	0.37	249.05	-267.144762	0.37
282.02	-267.144927	0.27	264.05	-267.144733	0.39
297.02	-267.145175	0.11	279.05	-267.144889	0.29
312.02	-267.145337	0.01	294.05	-267.145126	0.14
327.02	-267.145334	0.01	309.05	-267.145312	0.02
342.02	-267.145263	0.06	324.05	-267.145344	0.00
357.02	-267.145222	0.08	339.05	-267.145279	0.04
357.02	-267.145222	0.08	354.05	-267.145236	0.07

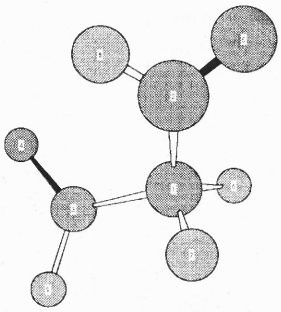
[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

[b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.



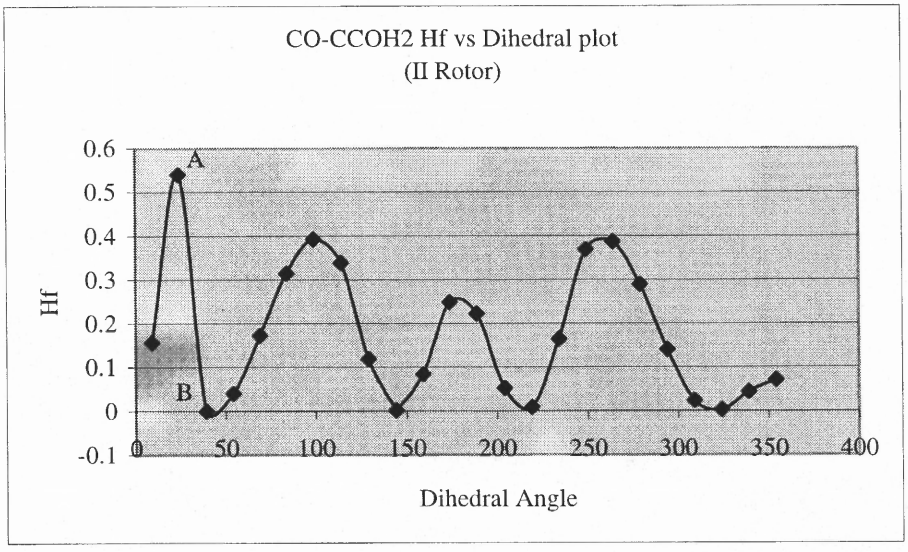


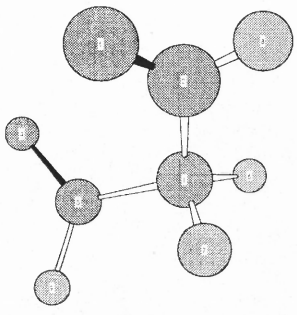
Structure at point A



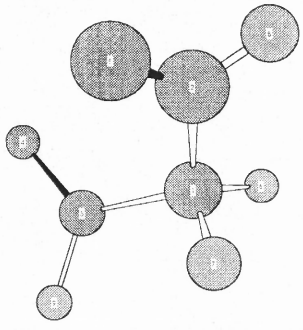
Structure at point B

Figure 2.27 Potential Barriers for Internal Rotation about CO-CCOH2 bond (Dihedral 4-3-1-2) of CCO2H2. Points are Calculated Values at non-relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.41 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*





Structure at point A



Structure at point B

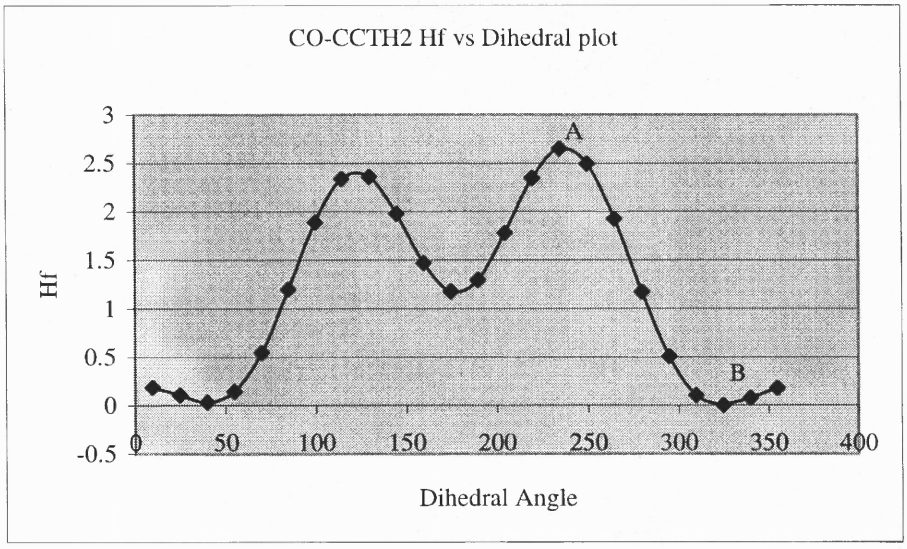
Figure 2.28 Potential Barriers for Internal Rotation about CO-CCOH2 bond (Dihedral 5-2-1-3) of CCO2H2. Points are Calculated Values at non-relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.41 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

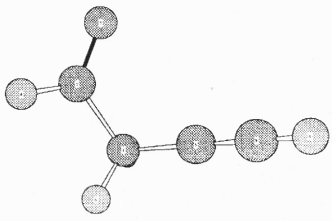
Table 2.42 Total Energy and Internal Rotation Barriers for CCOCTH2

	CO-CCTH2	
Torsion Angle	Total Energy [a]	Rotational barrier[b]
9.68	-229.967124	0.19
24.68	-229.967255	0.11
39.68	-229.96737	0.03
54.68	-229.967196	0.14
69.68	-229.966555	0.54
84.68	-229.965515	1.20
99.68	-229.964414	1.89
114.68	-229.963702	2.34
129.68	-229.963667	2.36
144.68	-229.96427	1.98
159.68	-229.965078	1.47
174.68	-229.965552	1.17
189.68	-229.965362	1.29
204.68	-229.964589	1.78
219.68	-229.96369	2.34
234.68	-229.963206	2.65
249.68	-229.963453	2.49
264.68	-229.964355	1.93
279.68	-229.965556	1.17
294.68	-229.96662	0.50
309.68	-229.967256	0.10
324.68	-229.967424	0.00
324.68	-229.967424	0.00
339.68	-229.967302	0.08
354.68	-229.967144	0.18

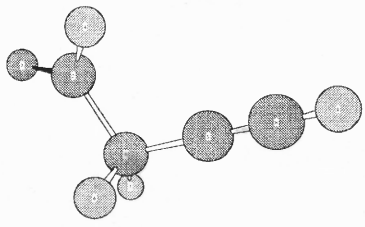
[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

[b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.





Structure at point A



Structure at point B

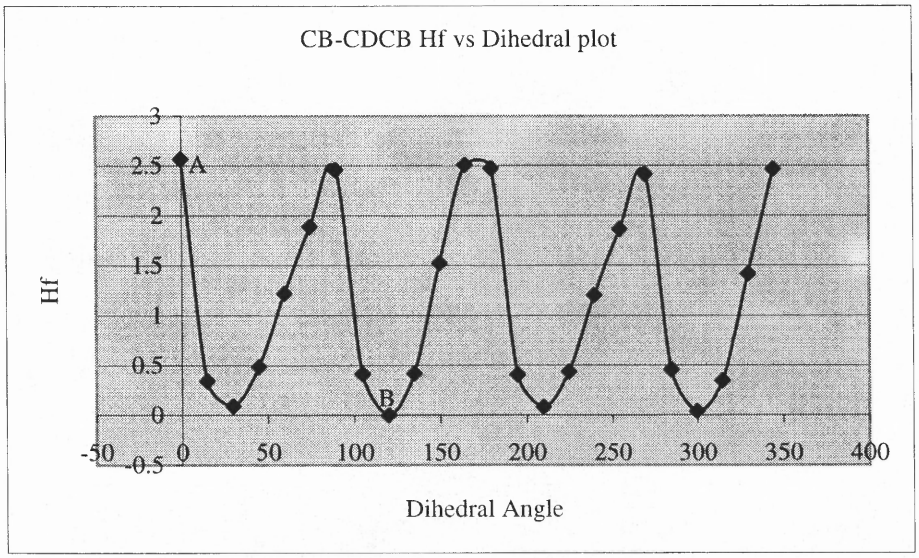
Figure 2.29 Potential Barriers for Internal Rotation about CO-CCTH2 bond (Dihedral 5-1-2-4) of CCOCTH2. Points are Calculated Values at relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.42 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

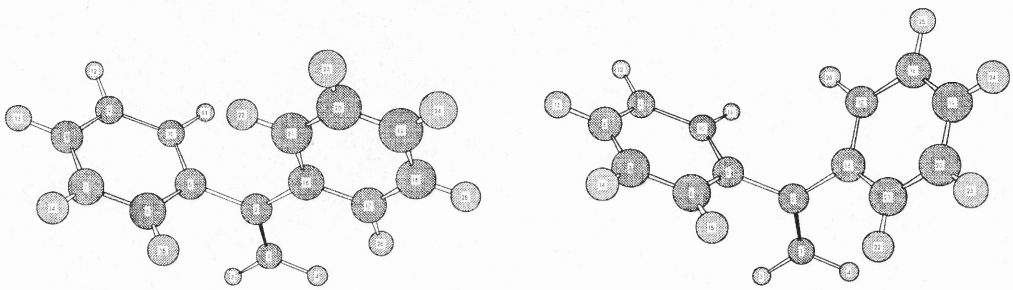
Table 2.43 Total Energy and Internal Rotation Barriers for CDCB2

CB-CDCB			CB-CDCB		
Torsion Angle	Total Energy [a]	Rotational barrier[b]	Torsion Angle	Total Energy [a]	Rotational barrier[b]
-0.41	-537.730048	2.57	0.00	-540.824434	3.79
14.59	-537.733599	0.34	10.00	-540.82213	5.23
29.59	-537.733997	0.09	20.00	-540.819631	6.80
44.59	-537.733365	0.49	30.00	-540.817139	8.36
59.59	-537.732203	1.22	40.00	-540.815826	9.19
74.59	-537.73113	1.89	50.00	-540.816989	8.46
89.59	-537.730226	2.46	60.00	-540.819896	6.63
104.59	-537.733485	0.41	70.00	-540.822671	4.89
119.59	-537.734141	0.00	80.00	-540.824422	3.79
134.59	-537.733481	0.41	90.00	-540.825511	3.11
149.59	-537.731711	1.52	100.00	-540.826539	2.47
164.59	-537.730148	2.51	110.00	-540.827691	1.74
179.59	-537.730197	2.47	120.00	-540.828931	0.96
194.59	-537.733492	0.41	130.00	-540.829974	0.31
209.59	-537.734015	0.08	140.00	-540.830467	0.00
224.59	-537.733448	0.43	150.00	-540.830145	0.20
239.59	-537.732228	1.20	160.00	-540.828818	1.03
254.59	-537.731169	1.86	170.00	-540.826734	2.34
269.59	-537.730296	2.41	180.00	-540.82441	3.80
284.59	-537.733417	0.45	190.00	-540.822012	5.31
299.59	-537.734078	0.04	200.00	-540.819412	6.94
314.59	-537.73359	0.35	210.00	-540.816849	8.55
329.59	-537.73188	1.42	220.00	-540.815541	9.37
344.59	-537.730213	2.46	230.00	-540.816787	8.58

[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

[b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.

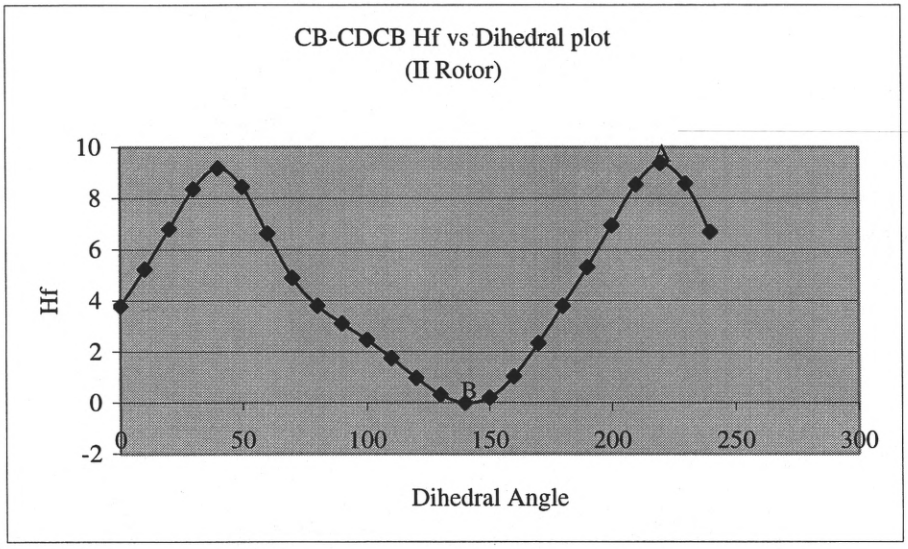


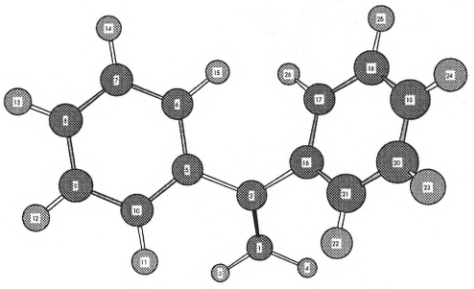


Structure at point A

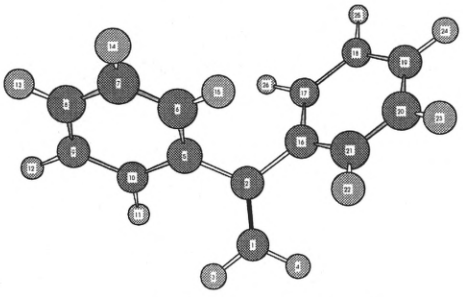
Structure at point B

Figure 2.30 Potential Barriers for Internal Rotation about CB-CDCB bond (Dihedral 17-16-1-2) of CDCB2. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.43 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*





Structure at point A



Structure at point B

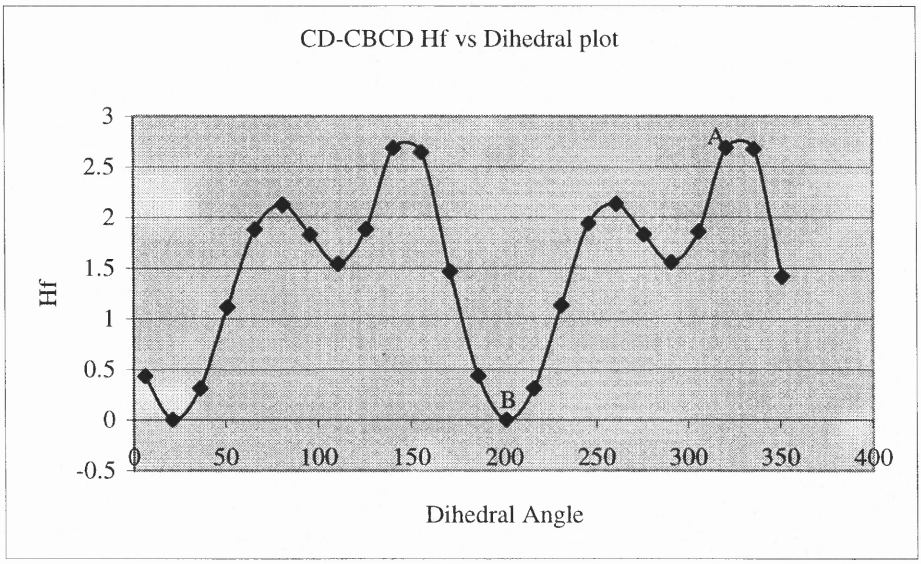
Figure 2.31 Potential Barriers for Internal Rotation about CB-CDCB bond (Dihedral 6-5-2-1) of CDCB2. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.43 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

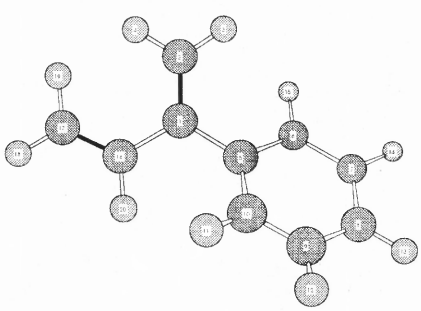
Table 2.44 Total Energy and Internal Rotation Barriers for CDCBCD

CB-CDCD		
Torsion Angle	Total Energy [a]	Rotational barrier[b]
6.03	-384.920858	0.43
21.03	-384.921547	0.00
36.03	-384.921051	0.31
51.03	-384.919771	1.11
66.03	-384.918551	1.88
81.03	-384.918163	2.12
96.03	-384.918634	1.83
111.03	-384.919094	1.54
126.03	-384.918548	1.88
141.03	-384.917269	2.68
156.03	-384.917339	2.64
171.03	-384.919211	1.47
186.03	-384.920854	0.44
201.03	-384.921548	0.00
216.03	-384.921051	0.31
231.03	-384.919739	1.14
246.03	-384.918456	1.94
261.03	-384.918146	2.13
276.03	-384.918634	1.83
291.03	-384.919066	1.56
306.03	-384.918582	1.86
321.03	-384.917266	2.69
336.03	-384.91729	2.67
351.03	-384.919288	1.42

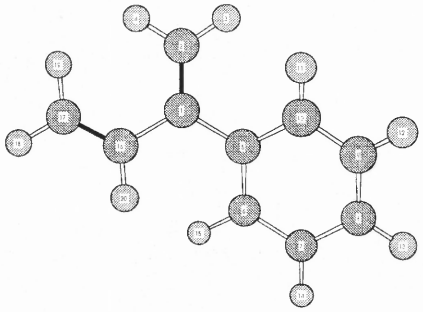
[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

[b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.





Structure at point A



Structure at point B

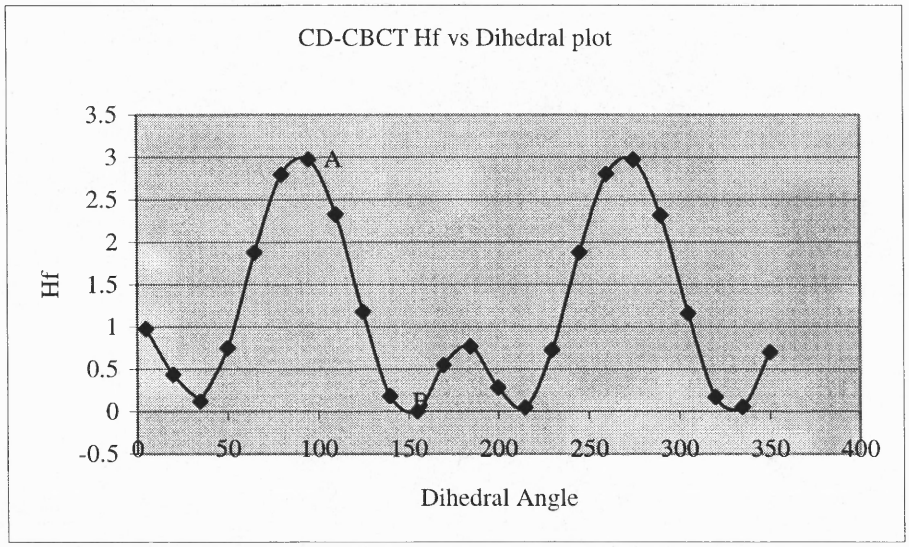
Figure 2.32 Potential Barriers for Internal Rotation about CD-CBCD bond (Dihedral 6-5-1-2) of CDCBCD. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.44 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

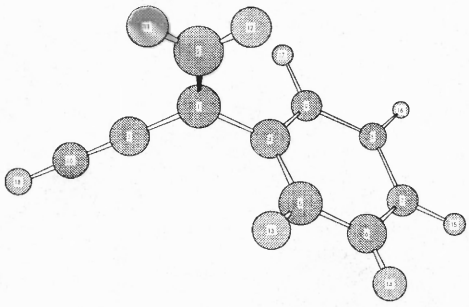
Table 2.45 Total Energy and Internal Rotation Barriers for CDCBCT

	CB-CDCT	
Torsion Angle	Total Energy [a]	Rotational barrier[b]
4.76	-385.786472	0.98
19.76	-385.787327	0.44
34.76	-385.787835	0.12
34.76	-385.787835	0.12
49.76	-385.786835	0.75
64.76	-385.785034	1.88
79.76	-385.783574	2.79
94.76	-385.783291	2.97
109.76	-385.784318	2.33
124.76	-385.786149	1.18
139.76	-385.787737	0.18
154.76	-385.788026	0.00
169.76	-385.787157	0.55
184.76	-385.786805	0.77
199.76	-385.787579	0.28
214.76	-385.787954	0.04
229.76	-385.786873	0.72
244.76	-385.785036	1.88
259.76	-385.783566	2.80
274.76	-385.783292	2.97
289.76	-385.784337	2.31
304.76	-385.786185	1.16
319.76	-385.787752	0.17
334.76	-385.787942	0.05
349.76	-385.786912	0.70

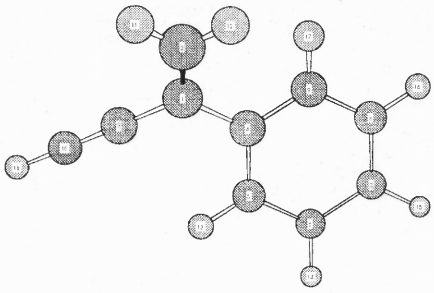
[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

[b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.





Structure at point A



Structure at point B

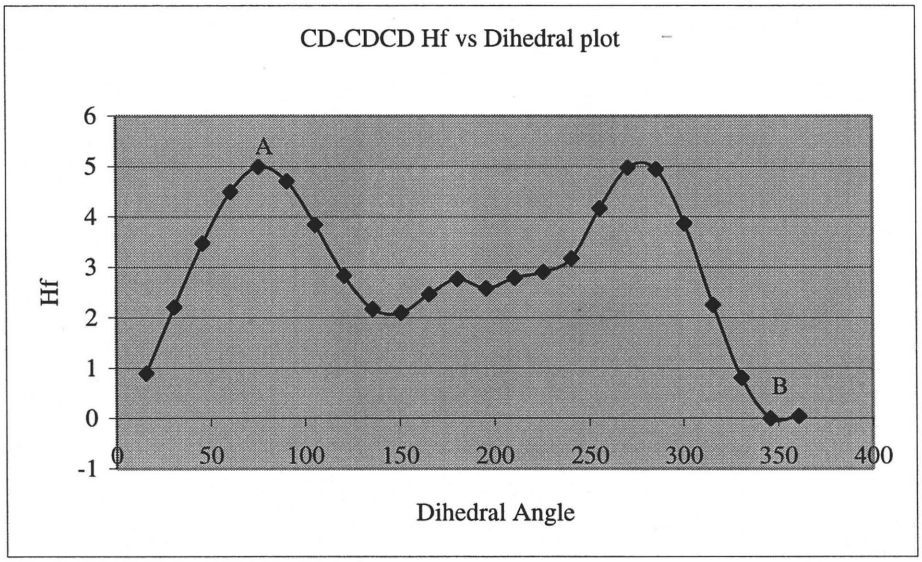
Figure 2.33 Potential Barriers for Internal Rotation about CD-CBCT bond (Dihedral 5-4-1-2) of CDCBCT. Points are Calculated Values at relaxed B3LYP/6-31G(d) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.45 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

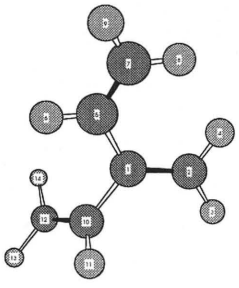
Table 2.46 Total Energy and Internal Rotation Barriers for CDCD2

CD-CDCD			CD-CDCD		
Torsion Angle	Total Energy [a]	Rotational barrier[b]	Torsion Angle	Total Energy [a]	Rotational barrier[b]
15.67	-232.109868	0.90	4.43	-233.394349	3.71
30.67	-232.107777	2.21	19.43	-233.391163	5.71
45.67	-232.105761	3.48	34.43	-233.397073	2.00
60.67	-232.104138	4.49	49.43	-233.396114	2.61
75.67	-232.103345	4.99	64.43	-233.395861	2.76
90.67	-232.103803	4.70	79.43	-233.396761	2.20
105.67	-232.10517	3.85	94.43	-233.398408	1.17
120.67	-232.106784	2.83	109.43	-233.3998	0.29
135.67	-232.107838	2.17	124.43	-233.400267	0.00
150.67	-232.107962	2.09	139.43	-233.399672	0.37
165.67	-232.107368	2.47	154.43	-233.398512	1.10
180.67	-232.106896	2.76	169.43	-233.398009	1.42
195.67	-232.107184	2.58	184.43	-233.399215	0.66
210.67	-232.10685	2.79	199.43	-233.400185	0.05
225.67	-232.106667	2.91	214.43	-233.400059	0.13
240.67	-232.106246	3.17	229.43	-233.398983	0.81
255.67	-232.104661	4.17	244.43	-233.397428	1.78
270.67	-232.103379	4.97	259.43	-233.396178	2.57
285.67	-232.103421	4.94	274.43	-233.396001	2.68
300.67	-232.105133	3.87	289.43	-233.396783	2.19
315.67	-232.107708	2.25	304.43	-233.397594	1.68
330.67	-232.110011	0.81	319.43	-233.398088	1.37
345.67	-232.111299	0.00	334.43	-233.398088	1.37
360.67	-232.11122	0.05	349.43	-233.396716	2.23

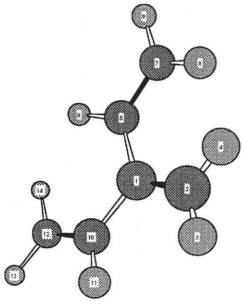
[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

[b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.



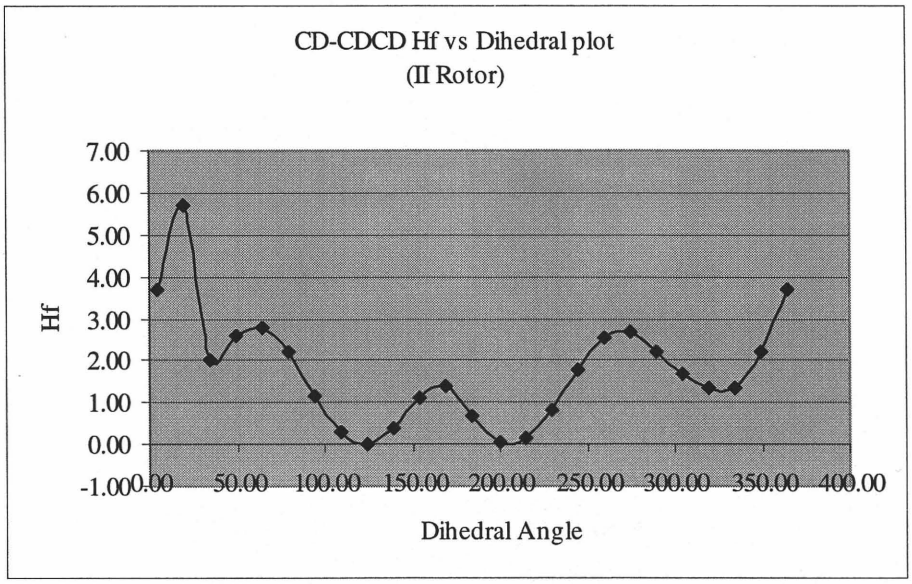


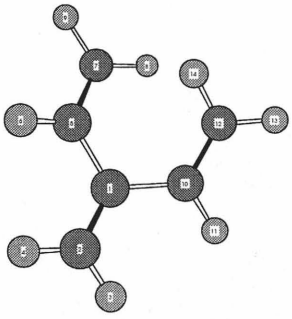
Structure at point A



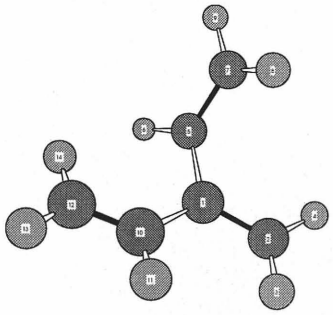
Structure at point B

Figure 2.34 Potential Barriers for Internal Rotation about CD-CDCD bond (Dihedral 11-10-1-2) of CDCD2. Points are Calculated Values at non-relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.46 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*





Structure at point A



Structure at point B

Figure 2.35 Potential Barriers for Internal Rotation about CD-CDCD bond (Dihedral 6-5-1-2) of CDCD2. Points are Calculated Values at non-relaxed B3LYP/6-31G(d,p) level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.46 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

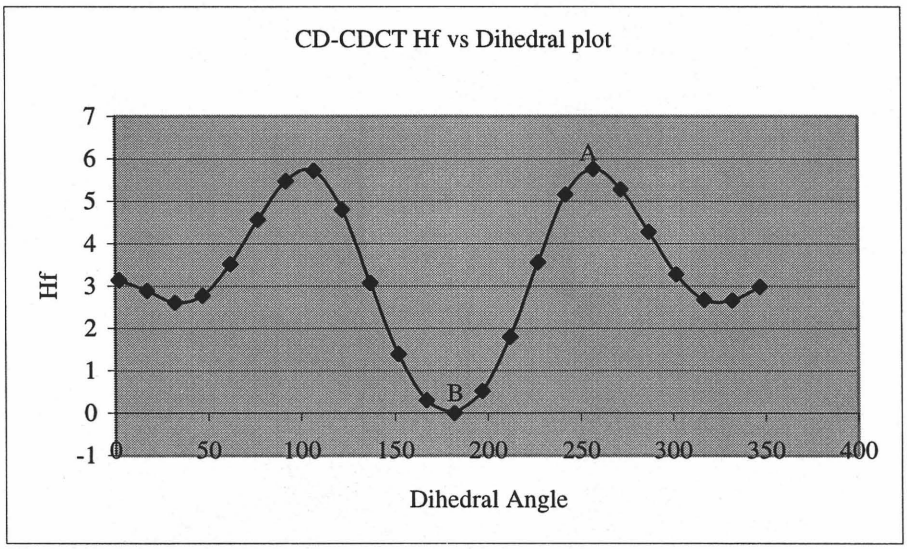
Table 2.47 Total Energy and Internal Rotation Barriers for CDCDCT

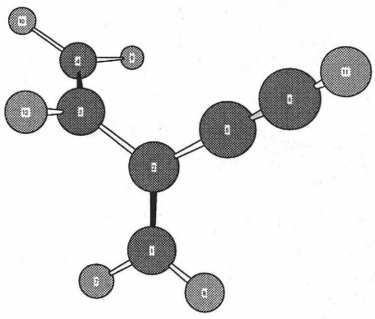
CD-CDCT

Torsion Angle	Total Energy [a]	Rotational barrier[b]
1.99	-230.859567	3.14
16.99	-230.859961	2.89
31.99	-230.860404	2.61
46.99	-230.86014	2.78
61.99	-230.858956	3.52
76.99	-230.857293	4.56
91.99	-230.855838	5.48
106.99	-230.855451	5.72
121.99	-230.856919	4.80
136.99	-230.859677	3.07
151.99	-230.862338	1.40
166.99	-230.864083	0.30
181.99	-230.864567	0.00
181.99	-230.864567	0.00
196.99	-230.863735	0.52
211.99	-230.861703	1.80
226.99	-230.858902	3.56
241.99	-230.856344	5.16
256.99	-230.855394	5.76
271.99	-230.856158	5.28
286.99	-230.857746	4.28
301.99	-230.859343	3.28
316.99	-230.860305	2.67
331.99	-230.860329	2.66
346.99	-230.859815	2.98

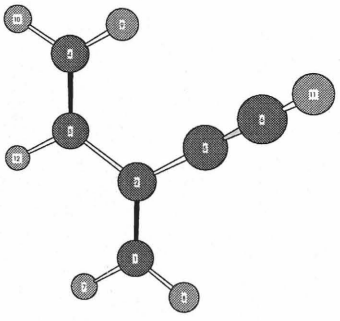
[a] Electronic energies at 0 K. ZPVE and Thermal correction to 298K are not included. Units in hartree.

[b] Rotational barriers are calculated as the difference between the total energy of each conformer and that of the most stable conformer. Units in kcal/mol.





Structure at point A



Structure at point B

Figure 2.36 Potential Barriers for Internal Rotation about CD-CDCT bond (Dihedral 4-3-2-1) of CDCDCT. Points are Calculated Values at non-relaxed B3LYP/3-21G level of theory. Potential Barrier is in kcal while Dihedral Angle is in Degrees. Refer to table 2.47 for Actual Energy Values. Further illustration of the specific dihedral of the Internal Rotation is in the specific table for structure parameters of the species (Tables 2.1 to 2.15). Note that Dihedral *a-b-c-d* infers rotation of angle of Atom *a* with respect to Atom *d* about Rotation Axis *c-b*

2.4.4 Entropy (S^{o}_{298}) and Heat Capacity ($C_p(T)$'s ($300 \leq T/K \leq 1500$))

S^{o}_{298} and $C_p(T)$'s calculation results using B3LYP/6-31G(d) determined geometries and frequencies are summarized in Table 2.65. TVR, represents the sum of the contributions from translations, external rotations and vibrations for S^{o}_{298} and $C_p(T)$'s. The torsion frequencies calculated for the internal rotors are not included in TVR. Instead, a more exact contribution from hindered rotations is calculated using the method of Pitzer and Gwinn.[17] I.R., represents the contributions from the internal rotation about C-C bond for S^{o}_{298} and $C_p(T)$'s. Translation, Vibration and External Rotation contributions to Entropy and Heat Capacity are calculated over the temperature range 298 K to 5000 K and represented in Tables 2.48 to 2.62. Table 2.47 shows the number of Internal Rotors, Symmetry and Moments of Inertia. Internal Rotation Contributions to Entropy and Heat Capacity are represented in Table 2.64.

Table 2.48 Number of Internal Rotors, Symmetry and Moments of Inertia[a,b] used in the estimation of contributions to Entropy[c] and Heat Capacity[c]

Species	Formula	Rotors	Molecular Wt.	I_a	I_b	I_c	Symmetry
CCB2H2	C13H12	2	168	874.54	4363.73	4396.75	8
CCBCDH2	C9H10	2	118	427.78	1859.67	2187.07	2
CCBCOH2	C8H8O	2	120	442.18	1844.95	2123.22	2
CCBCTH2	C9H8	1	116	415.76	1743.27	2141.93	2
CCD2H2	C5H8	2	68	90.39	773.85	779.82	2
CCDCOH2	C4H6O	2	70	90.34	743.24	751.16	1
CCO2H2	C3H4O2	2	72	121.93	596.56	684.03	2
CCOCTH2	C4H4O	1	68	70.95	717.00	761.49	1
CCT2H2	C5H4	0	64	94.54	637.33	720.83	2
CDCB2	C14H12	2	180	1124.62	4371.24	4986.43	8
CDCBCD	C10H10	1	130	575.63	2094.66	2583.37	2
CDCBCT	C10H8	1	128	637.59	1886.77	2460.12	2
CDCD2	C6H8	2	80	322.54	634.56	927.28	2
CDCDCT	C6H6	1	78	380.54	513.76	894.30	1
CDCT2	C6H4	0	76	290.82	634.53	925.36	2

[a] Optimized at the B3LYP/6-31G(d) level of theory.

[b] Units in amu-Bohr^2.

[c] Multiplicity of all species is 1, Spin of all species is 0, Number of Optical Isomers for all species is 1

Table 2.49 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CCB2H2 at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	39.04	89.14	5.94
300	39.36	89.40	6.02
400	54.45	102.84	10.72
500	67.42	116.45	16.82
600	77.96	129.72	24.10
700	86.49	142.42	32.33
800	93.49	154.46	41.34
900	99.32	165.83	50.97
1000	104.23	176.57	61.15
1100	108.41	186.72	71.78
1200	111.98	196.32	82.79
1300	115.05	205.42	94.13
1400	117.70	214.06	105.76
1500	120.00	222.27	117.64
1600	122.00	230.09	129.73
1700	123.75	237.56	142.00
1800	125.28	244.68	154.44
1900	126.63	251.50	167.03
2000	127.83	258.04	179.74
2500	132.10	287.11	244.75
3000	134.64	311.47	311.42
3500	136.26	332.38	379.10
4000	137.34	350.68	447.45
4500	138.10	366.92	516.25
5000	138.65	381.53	585.37

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.50 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CCBCDH2 at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	28.85	79.37	4.65
300	29.07	79.56	4.71
400	39.78	89.42	8.15
500	49.11	99.35	12.61
600	56.79	109.02	17.91
700	63.09	118.27	23.91
800	68.31	127.06	30.48
900	72.71	135.38	37.53
1000	76.44	143.25	44.98
1100	79.65	150.70	52.79
1200	82.40	157.76	60.88
1300	84.78	164.46	69.24
1400	86.85	170.83	77.81
1500	88.64	176.89	86.58
1600	90.21	182.67	95.52
1700	91.58	188.19	104.60
1800	92.79	193.46	113.81
1900	93.85	198.52	123.13
2000	94.79	203.36	132.56
2500	98.18	224.94	180.83
3000	100.19	243.06	230.41
3500	101.47	258.63	280.79
4000	102.33	272.26	331.71
4500	102.94	284.36	382.98
5000	103.38	295.25	434.51

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.51 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CCBCOH2 at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	26.98	80.00	4.47
300	27.17	80.18	4.53
400	36.66	89.32	7.72
500	44.92	98.43	11.81
600	51.72	107.25	16.65
700	57.29	115.67	22.11
800	61.89	123.64	28.06
900	65.74	131.16	34.45
1000	68.99	138.27	41.18
1100	71.76	144.99	48.21
1200	74.13	151.35	55.50
1300	76.17	157.37	63.01
1400	77.93	163.09	70.71
1500	79.46	168.53	78.58
1600	80.78	173.71	86.58
1700	81.94	178.64	94.71
1800	82.96	183.36	102.95
1900	83.85	187.88	111.28
2000	84.64	192.21	119.70
2500	87.47	211.45	162.75
3000	89.15	227.58	206.89
3500	90.21	241.43	251.71
4000	90.93	253.54	296.96
4500	91.43	264.30	342.51
5000	91.79	273.96	388.27

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.52 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CCBCTH2 at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	30.34	81.47	5.01
300	30.55	81.67	5.07
400	40.09	91.81	8.61
500	48.12	101.66	13.03
600	54.63	111.04	18.17
700	59.94	119.88	23.90
800	64.32	128.19	30.12
900	68.01	136.00	36.73
1000	71.14	143.34	43.69
1100	73.83	150.26	50.93
1200	76.13	156.79	58.42
1300	78.13	162.98	66.13
1400	79.86	168.84	74.03
1500	81.36	174.41	82.08
1600	82.68	179.71	90.28
1700	83.83	184.76	98.59
1800	84.84	189.59	107.02
1900	85.74	194.21	115.54
2000	86.53	198.63	124.15
2500	89.37	218.30	168.14
3000	91.06	234.78	213.24
3500	92.14	248.92	259.01
4000	92.87	261.29	305.23
4500	93.38	272.28	351.75
5000	93.75	282.15	398.49

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.53 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CCD2H2 at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	18.67	67.74	3.43
300	18.80	67.87	3.47
400	25.11	74.15	5.66
500	30.80	80.39	8.46
600	35.61	86.45	11.79
700	39.66	92.26	15.55
800	43.11	97.79	19.69
900	46.08	103.05	24.15
1000	48.64	108.05	28.89
1100	50.87	112.80	33.86
1200	52.81	117.32	39.04
1300	54.51	121.62	44.41
1400	55.99	125.72	49.93
1500	57.28	129.63	55.59
1600	58.41	133.37	61.37
1700	59.41	136.94	67.25
1800	60.29	140.37	73.23
1900	61.07	143.66	79.30
2000	61.76	146.81	85.43
2500	64.24	160.90	116.96
3000	65.73	172.77	149.45
3500	66.69	183.00	182.54
4000	67.33	191.96	216.02
4500	67.78	199.92	249.77
5000	68.10	207.09	283.71

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.54 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CCDCOH2 at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	16.80	68.30	3.26
300	16.91	68.41	3.29
400	21.98	73.98	5.23
500	26.60	79.40	7.67
600	30.54	84.61	10.53
700	33.86	89.58	13.75
800	36.69	94.30	17.28
900	39.11	98.77	21.07
1000	41.19	103.01	25.08
1100	42.99	107.02	29.29
1200	44.55	110.84	33.66
1300	45.90	114.46	38.18
1400	47.07	117.91	42.83
1500	48.09	121.20	47.58
1600	48.99	124.33	52.43
1700	49.77	127.33	57.37
1800	50.46	130.20	62.37
1900	51.07	132.95	67.45
2000	51.61	135.59	72.58
2500	53.54	147.34	98.88
3000	54.69	157.23	125.94
3500	55.43	165.73	153.46
4000	55.92	173.17	181.27
4500	56.27	179.79	209.30
5000	56.52	185.74	237.47

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.55 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CCOCTH2 at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	18.33	70.23	3.62
300	18.41	70.35	3.65
400	22.34	76.20	5.70
500	25.66	81.56	8.10
600	28.42	86.50	10.81
700	30.75	91.06	13.76
800	32.73	95.31	16.94
900	34.44	99.27	20.30
1000	35.92	102.98	23.81
1100	37.19	106.47	27.47
1200	38.30	109.76	31.24
1300	39.26	112.87	35.12
1400	40.10	115.81	39.08
1500	40.83	118.61	43.13
1600	41.47	121.27	47.24
1700	42.04	123.80	51.41
1800	42.53	126.22	55.64
1900	42.97	128.53	59.91
2000	43.35	130.75	64.22
2500	44.74	140.60	86.25
3000	45.57	148.85	108.83
3500	46.10	155.92	131.74
4000	46.46	162.11	154.86
4500	46.71	167.61	178.13
5000	46.89	172.54	201.51

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.56 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CCT2H2 at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	21.49	71.55	4.10
300	21.58	71.70	4.15
400	25.60	78.49	6.51
500	28.72	84.55	9.23
600	31.21	90.02	12.23
700	33.30	95.00	15.46
800	35.08	99.57	18.88
900	36.64	103.80	22.46
1000	38.00	107.74	26.19
1100	39.20	111.42	30.05
1200	40.25	114.89	34.02
1300	41.18	118.15	38.09
1400	41.99	121.23	42.24
1500	42.71	124.16	46.48
1600	43.34	126.94	50.78
1700	43.89	129.59	55.13
1800	44.39	132.11	59.54
1900	44.82	134.53	64.00
2000	45.21	136.84	68.50
2500	46.62	147.11	91.47
3000	47.48	155.70	114.99
3500	48.02	163.07	138.85
4000	48.39	169.52	162.94
4500	48.65	175.24	187.18
5000	48.84	180.38	211.53

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.57 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CDCBCT at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	33.81	85.02	5.47
300	34.03	85.24	5.54
400	44.35	96.50	9.47
500	52.81	107.35	14.33
600	59.58	117.62	19.96
700	65.04	127.24	26.20
800	69.54	136.24	32.92
900	73.31	144.66	40.07
1000	76.50	152.57	47.55
1100	79.24	160.00	55.34
1200	81.59	167.01	63.37
1300	83.63	173.63	71.63
1400	85.40	179.90	80.07
1500	86.94	185.86	88.68
1600	88.28	191.52	97.44
1700	89.46	196.91	106.31
1800	90.49	202.06	115.30
1900	91.41	206.99	124.39
2000	92.22	211.71	133.56
2500	95.14	232.66	180.42
3000	96.88	250.19	228.42
3500	98.00	265.24	277.11
4000	98.75	278.39	326.25
4500	99.27	290.07	375.72
5000	99.65	300.57	425.40

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.58 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CDCDCT at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	23.51	75.14	4.21
300	23.64	75.30	4.25
400	29.60	82.96	6.92
500	34.45	90.11	10.13
600	38.37	96.76	13.78
700	41.60	102.93	17.78
800	44.33	108.67	22.07
900	46.67	114.04	26.62
1000	48.69	119.07	31.39
1100	50.46	123.80	36.34
1200	52.00	128.26	41.46
1300	53.35	132.49	46.73
1400	54.53	136.49	52.12
1500	55.57	140.29	57.62
1600	56.48	143.91	63.21
1700	57.28	147.37	68.90
1800	57.99	150.67	74.66
1900	58.62	153.82	80.48
2000	59.18	156.85	86.37
2500	61.21	170.31	116.48
3000	62.43	181.60	147.39
3500	63.21	191.30	178.78
4000	63.74	199.79	210.49
4500	64.11	207.33	242.43
5000	64.38	214.10	274.52

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.59 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CDCT2 at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	24.87	75.73	4.53
300	24.98	75.89	4.58
400	29.82	83.79	7.33
500	33.39	90.85	10.50
600	36.15	97.20	13.98
700	38.41	102.95	17.71
800	40.31	108.22	21.64
900	41.95	113.07	25.75
1000	43.38	117.57	30.02
1100	44.63	121.77	34.41
1200	45.73	125.70	38.93
1300	46.70	129.41	43.55
1400	47.55	132.91	48.26
1500	48.29	136.22	53.05
1600	48.95	139.36	57.90
1700	49.54	142.35	62.82
1800	50.05	145.20	67.80
1900	50.51	147.92	72.82
2000	50.92	150.52	77.89
2500	52.41	162.08	103.73
3000	53.31	171.73	130.15
3500	53.88	180.00	156.93
4000	54.27	187.23	183.95
4500	54.55	193.65	211.14
5000	54.75	199.42	238.44

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.60 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CCO2H2 at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	15.11	66.62	3.14
300	15.19	66.73	3.17
400	19.03	71.63	4.88
500	22.54	76.26	6.96
600	25.58	80.65	9.37
700	28.16	84.80	12.06
800	30.35	88.71	14.98
900	32.21	92.40	18.11
1000	33.81	95.88	21.41
1100	35.17	99.18	24.86
1200	36.34	102.29	28.43
1300	37.34	105.24	32.11
1400	38.21	108.05	35.89
1500	38.96	110.71	39.75
1600	39.61	113.25	43.67
1700	40.17	115.67	47.66
1800	40.67	117.98	51.70
1900	41.11	120.20	55.78
2000	41.49	122.32	59.91
2500	42.86	131.75	81.01
3000	43.67	139.65	102.64
3500	44.18	146.43	124.59
4000	44.53	152.37	146.76
4500	44.77	157.63	169.06
5000	44.94	162.36	191.47

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.61 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CDCB2 at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	42.65	90.92	6.46
300	42.98	91.20	6.54
400	58.77	105.79	11.64
500	72.16	120.42	18.20
600	82.95	134.58	25.97
700	91.64	148.06	34.71
800	98.74	160.79	44.23
900	104.65	172.79	54.39
1000	109.62	184.10	65.10
1100	113.84	194.76	76.27
1200	117.46	204.84	87.83
1300	120.57	214.38	99.72
1400	123.25	223.43	111.90
1500	125.58	232.03	124.33
1600	127.61	240.21	136.98
1700	129.39	248.01	149.82
1800	130.94	255.46	162.83
1900	132.32	262.59	175.98
2000	133.53	269.42	189.26
2500	137.88	299.77	257.14
3000	140.47	325.19	326.70
3500	142.12	347.01	397.31
4000	143.22	366.09	468.58
4500	144.00	383.03	540.32
5000	144.56	398.25	612.39

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.62 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CDCBCD at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	34.32	86.25	5.58
300	34.56	86.48	5.65
400	46.02	98.04	9.69
500	55.79	109.40	14.79
600	63.73	120.32	20.77
700	70.18	130.65	27.47
800	75.52	140.40	34.76
900	80.00	149.57	42.53
1000	83.80	158.21	50.72
1100	87.06	166.37	59.26
1200	89.86	174.08	68.10
1300	92.28	181.38	77.20
1400	94.38	188.30	86.53
1500	96.21	194.89	96.05
1600	97.81	201.16	105.74
1700	99.20	207.14	115.58
1800	100.44	212.85	125.55
1900	101.52	218.32	135.64
2000	102.48	223.56	145.83
2500	105.94	246.87	197.97
3000	108.00	266.41	251.44
3500	109.32	283.18	305.74
4000	110.20	297.86	360.57
4500	110.82	310.90	415.78
5000	111.27	322.62	471.25

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.63 Translation,Vibration and External Rotation contribution to Entropy and Heat Capacity for CDCD2 at different temperatures

T[a]	Cp[b]	S[c]	[H(T)-H(0K)][d]
298	22.12	71.75	3.87
300	22.26	71.90	3.91
400	29.33	79.30	6.50
500	35.45	86.53	9.74
600	40.53	93.47	13.55
700	44.75	100.05	17.81
800	48.31	106.27	22.47
900	51.36	112.15	27.45
1000	53.99	117.70	32.72
1100	56.28	122.97	38.23
1200	58.27	127.96	43.95
1300	60.00	132.70	49.86
1400	61.52	137.21	55.93
1500	62.85	141.50	62.15
1600	64.01	145.60	68.48
1700	65.04	149.52	74.93
1800	65.94	153.27	81.47
1900	66.74	156.86	88.10
2000	67.45	160.31	94.81
2500	70.02	175.68	129.20
3000	71.56	188.61	164.59
3500	72.54	199.73	200.59
4000	73.20	209.48	237.01
4500	73.67	218.14	273.69
5000	74.01	225.93	310.58

[a] Temperature in Kelvin
[b] Heat Capacity in cal/mol/K
[c] Entropy in cal/mol/K
[d] Enthalpy in kcal/mol

Table 2.64 Internal Rotor Contributions to Entropy and Heat Capacity for Each Species

Species	Rotor	S^{o}_{298} [a]	Cp300 [b]	Cp400	Cp500	Cp600	Cp800	Cp1000	Cp1500
CCB2H2		16.34	3.35	2.97	2.71	2.53	2.32	2.21	2.09
	C6H5-CH2C6H5	8.52	1.24	1.14	1.09	1.06	1.03	1.02	1.00
	C6H5-CH2C6H5	7.83	2.12	1.84	1.62	1.47	1.29	1.19	1.09
CCBCDH2		12.81	4.51	4.36	4.08	3.79	3.29	2.94	2.48
	C6H5-CH2C2H3	7.09	2.26	2.04	1.82	1.65	1.42	1.29	1.13
	C2H3-CH2C6H5	5.72	2.25	2.32	2.26	2.14	1.87	1.66	1.35
CCBCOH2		12.15	4.35	4.21	4.07	3.95	3.72	3.47	2.93
	C6H5-CH2CHO	5.77	2.10	2.19	2.27	2.32	2.31	2.19	1.81
	CHO-CH2C6H5	6.38	2.25	2.02	1.80	1.63	1.41	1.28	1.13
CCBCTH2		8.07	1.10	1.05	1.03	1.02	1.01	1.00	1.00
	C6H5-CH2C2H	8.07	1.10	1.05	1.03	1.02	1.01	1.00	1.00
CCD2H2		12.63	4.38	3.92	3.51	3.18	2.75	2.51	2.23
	CH2(C2H3)-C2H3	6.12	2.29	2.12	1.91	1.73	1.48	1.33	1.15
	CH2(C2H3)-C2H3	6.51	2.09	1.80	1.60	1.45	1.28	1.18	1.08
CCDCOH2		12.23	4.54	4.21	3.80	3.44	2.95	2.66	2.31
	CHO-CH2C2H3	6.17	2.25	2.05	1.84	1.66	1.43	1.30	1.14
	C2H3-CH2CHO	6.06	2.29	2.16	1.96	1.78	1.52	1.37	1.17
CCO2H2		14.31	2.43	2.25	2.16	2.11	2.06	2.04	2.01
	CHO-CH2CHO	7.13	1.26	1.15	1.10	1.07	1.04	1.02	1.01
	CHO-CH2CHO	7.18	1.18	1.10	1.06	1.04	1.02	1.01	1.00
CCOCTH2		5.97	2.31	2.17	1.97	1.79	1.53	1.37	1.18
	CHO-CH2C2H	5.97	2.31	2.17	1.97	1.79	1.53	1.37	1.18
CDCB2 [c]		7.40	2.30	2.15	1.95	1.76	1.51	1.35	1.17
	C6H5-C(CH2)C6H	7.40	2.30	2.15	1.95	1.76	1.51	1.35	1.17
CDCBCD [c]		6.95	2.31	2.18	1.99	1.81	1.54	1.38	1.18
	C6H5-C(CH2)C2H3	6.95	2.31	2.18	1.99	1.81	1.54	1.38	1.18
CDCBCT		6.77	2.34	2.26	2.09	1.91	1.63	1.45	1.22
	C6H5-C(CH2)C2H	6.77	2.34	2.26	2.09	1.91	1.63	1.45	1.22
CDCD2		10.37	4.20	4.47	4.61	4.61	4.35	3.96	3.19
	C2H3-C(CH2)C2H	5.24	2.17	2.28	2.33	2.31	2.13	1.92	1.54
	C2H3-C(CH2)C2H	5.13	2.03	2.18	2.27	2.31	2.22	2.04	1.65
CDCDCT		5.06	2.12	2.23	2.31	2.33	2.24	2.06	1.66
	C2H3-C(CH2)C2H	5.06	2.12	2.23	2.31	2.33	2.24	2.06	1.66

[a] Units in kcal/mol

[b] Units in cal/mol/K

[c] Only one Internal Rotor considered here, the second internal rotor was found to have a very high Rotation Barrier during calculations, which are suspected to be erroneous. The torsion frequency for this rotor has been used instead of the internal rotation contribution.

Table 2.65 Ideal Gas-phase Thermodynamic Properties[a,m]

Species	Symmetry	$\Delta H_{f\,298}^{o}$ [b]	S_{298}^{o} [c]	Cp300[c]	Cp400	Cp500	Cp600	Cp800	Cp1000	Cp1500
CCB2H2	8	42.41	105.48	42.71	57.42	70.13	80.49	95.81	106.44	122.09
TVR [d]			89.14	39.36	54.45	67.42	77.96	93.49	104.23	120.00
I.R.[e]			16.34	3.35	2.97	2.71	2.53	2.32	2.21	2.09
Literature		39.39[g]	104[h]							
CCBCDH2	2	34.70	92.18	33.58	44.14	53.19	60.58	71.60	79.38	91.12
TVR [d]			79.37	29.07	39.78	49.11	56.79	68.31	76.44	88.64
I.R.[e]			12.81	4.51	4.36	4.08	3.79	3.29	2.94	2.48
CCBCOH2	2	-13.35	92.15	31.52	40.87	48.99	55.67	65.61	72.45	82.38
TVR [d]			80.00	27.17	36.66	44.92	51.72	61.89	68.99	79.45
I.R.[e]			12.15	4.35	4.21	4.07	3.95	3.72	3.46	2.93
CCBCTH2	2	74.70	89.54	31.64	41.14	49.15	55.65	65.33	72.14	82.36
TVR [d]			81.47	30.54	40.09	48.12	54.63	64.32	71.14	81.36
I.R.[e]			8.07	1.10	1.05	1.03	1.02	1.01	1.00	1.00
CCD2H2	2	27.08	80.37	23.18	29.03	34.31	38.79	45.86	51.15	59.52
TVR [d]			67.74	18.80	25.11	30.80	35.61	43.11	48.64	57.28
I.R.[e]			12.63	4.38	3.92	3.51	3.18	2.75	2.51	2.24
Literature		25.41[i]	79.821[j]	23.6[k]	30.09	35.83	40.66	48.16	53.61	62.00
CCDCOH2	1	-20.68	80.53	21.45	26.19	30.40	33.98	39.64	43.85	50.40
TVR [d]			68.30	16.91	21.98	26.60	30.54	36.69	41.19	48.09
I.R.[e]			12.23	4.54	4.21	3.80	3.44	2.95	2.66	2.31
CCO2H2	2	-64.88	80.93	17.61	21.28	24.70	27.69	32.41	35.85	40.97
TVR [d]			66.62	15.18	19.03	22.54	25.58	30.35	33.81	38.96
I.R.[e]			14.31	2.43	2.25	2.16	2.11	2.06	2.04	2.01
CCOCTH2	1	19.72	76.20	20.72	24.51	27.63	30.21	34.26	37.29	42.01
TVR [d]			70.23	18.41	22.34	25.66	28.42	32.73	35.92	40.83
I.R.[e]			5.97	2.31	2.17	1.97	1.79	1.53	1.37	1.18
CCT2H2	2	112.43	71.55	21.58	25.60	28.72	31.21	35.08	38.00	42.71
TVR [d]			71.55	21.58	25.60	28.72	31.21	35.08	38.00	42.71
CDCB2	8	60.86	102.67	47.25	62.90	76.09	86.69	102.23	112.95	128.74
TVR [d]			95.27	44.95	60.75	74.14	84.93	100.72	111.60	127.57
I.R.[e,l]			7.40	2.30	2.15	1.95	1.76	1.51	1.35	1.17
CDCBCD	2	53.41	93.20	36.87	48.20	57.78	65.53	77.06	85.18	97.39
TVR [d]			86.25	34.56	46.02	55.79	63.72	75.52	83.80	96.21
I.R.[e,l]			6.95	2.31	2.18	1.99	1.81	1.54	1.38	1.18
CDCBCT	2	94.96	91.79	36.37	46.61	54.90	61.49	71.17	77.95	88.15
TVR [d]			85.02	34.03	44.35	52.81	59.58	69.54	76.50	86.93
I.R.[e]			6.77	2.34	2.26	2.09	1.91	1.63	1.45	1.22

Table 2.65 Ideal Gas-phase Thermodynamic Properties[a,e] (Continued)

Species	Symmetry	$\Delta H_f^\circ{}_{298}$[b]	$S^\circ{}_{298}$[c]	Cp300[c]	Cp400	Cp500	Cp600	Cp800	Cp1000	Cp1500
CDCD2	2	48.68	82.12	26.46	33.80	40.06	45.14	52.66	57.95	66.04
TVR[d]			71.75	22.26	29.33	35.45	40.53	48.31	53.99	62.85
I.R.[e]			10.37	4.20	4.47	4.61	4.61	4.35	3.96	3.19
CDCDCT	1	85.45	80.20	25.76	31.83	36.76	40.70	46.56	50.75	57.23
TVR[d]			75.14	23.64	29.60	34.45	38.37	44.32	48.69	55.57
I.R.[e]			5.06	2.12	2.23	2.31	2.33	2.24	2.06	1.66
CDCT2	2	131.68	75.73	24.98	29.82	33.39	36.15	40.31	43.38	48.29
TVR[d]			75.73	24.98	29.82	33.39	36.15	40.31	43.38	48.29

[a] Thermodynamic properties are referred to a standard state of an ideal gas at 1 atm.
[b] Units in kcal/mol.
[c] Units in cal/mol.K.
[d] The sum of contributions from translations, external rotations, and vibrations.
[e] Contribution from internal rotations.
[f] Symmetry number is taken into account (–Rln(symmetry number)).
[g] Reference 44
[h] Reference 45
[i] Reference 42
[j] Reference 43
[k] Reference 44, for all Cp values, shown as literature reference.
[l] Only one Internal Rotor considered here, the second internal rotor was found to have a very high Rotation Barrier during calculations, which are suspected to be erroneous. The torsion frequency for this rotor has been used instead of the internal rotation contribution.
[m] CDCT2 and CCT2H2 do not have any internal rotors and hence no contributions from Internal Rotors to Entropy and Heat Capacity.

2.4.5 Group Additivity Values

Group additivity[27] is a straightforward and reasonably accurate calculation method to estimate thermodynamic properties of hydrocarbons and oxygenated hydrocarbons;[28] modifications have also been reported that make it useful for chlorinated and fluorinated hydrocarbons.[29,30,31,32] In this work a set of hydrocarbon and oxy hydrocarbon groups has been derived from the thermodynamic property data of the calculated species.

For example values are reported for the group C/CB/CD/H2 derived from CCBCDH2.

$\Delta H_f^{\circ}{}_{298}$ and C_P's of C/CB/CD/H2 are calculated on the basis of

$$CCBCDH2 = (C/CB/CD/H2) + (CB/C) + 5(CB/H) + (CD/C/H) + (CD/H2)$$

$S^{\circ}{}_{298}$ of C/CB/CD/H2 is calculated on the basis of

$$CCBCDH2 = (C/CB/CD/H2) + (CB/C) + 5(CB/H) + (CD/C/H) + (CD/H2) + R\ln(\sigma) + OI$$

where R = 1.987 cal/mol.K, σ is symmetry number, and OI stand for optical isomer group. The group values of other groups are estimated in the same manner, each one derived from one species calculated in this work. Selection of the initial group values is critical to development of group additivity for accurate property estimation. These criteria are fully discussed in reference 29 and 30. The group values for $\Delta H_f^{\circ}{}_{298}$, $S^{\circ}{}_{298}$, and C_p (T) of all the groups not calculated in this work are taken from the existing literature value.[28,33] The parameters used in calculating Group Values are shown in Table 2.65. All the group values are derived in this work are listed in Table 2.66.

Table 2.66 Groups (for Group Additivity[a,b]) and Structure Parameters for Species

Species	Group #	Group ID	Quantity	No. of Internal Rotors	Symmetry
CCB2H2	1	CB/C	2	2	8
	2	CB/H	10		
	3	C/CB2/H2	1		
CCBCDH2	1	CB/C	1	2	2
	2	CB/H	5		
	3	CD/C/H	1		
	4	CD/H2	1		
	5	C/CB/CD/H2	1		
CCBCOH2	1	CB/C	1	2	2
	2	CB/H	5		
	3	CO/C/H	1		
	4	C/CB/CO/H2	1		
CCBCTH2	1	CB/C	1	1	2
	2	CB/H	5		
	3	CT/C	1		
	4	CT/H	1		
	5	C/CB/CT/H2	1		
CCD2H2	1	CD/H2	2	2	2
	2	CD/C/H	2		
	3	C/CD2/H2	1		
CCDCOH2	1	CD/H2	1	2	1
	2	CD/C/H	1		
	3	CO/C/H	1		
	4	C/CD/CO/H2	1		
CCO2H2	1	CO/C/H	2	2	2
	2	C/CO2/H2	1		
CCOCTH2	1	CT/H	1	1	1
	2	CT/C	1		
	3	CO/C/H	1		
	4	C/CO/CT/H2	1		
CCT2H2	1	CT/C	2	0	2
	2	CT/H	2		
	3	C/CT2/H2	1		
CDCB2	1	CB/CD	2	2	8
	2	CB/H	10		
	3	CD/H2	1		
	4	CD/CB2	1		
CDCBCD	1	CD/H2	2	1	2
	2	CD/CD/H	1		
	3	CB/CD	1		
	4	CB/H	5		
	5	CD/CB/CD	1		

Table 2.66 Groups (for Group Additivity[a,b]) and Structure Parameters for Species (Continued)

Species	Group #	Group ID	Quantity	No. of Internal Rotors	Symmetry
CDCBCT		1	CT/H	1	1 2
		2	CT/CD	1	
		3	CB/CD	1	
		4	CD/H2	1	
		5	CB/H	5	
		6	CD/CB/CT	1	
CDCD2		1	CD/H2	3	2 2
		2	CD/CD/H	2	
		3	CD/CD2	1	
CDCDCT		1	CT/H	1	1 1
		2	CT/CD	1	
		3	CD/CD/H	1	
		4	CD/H2	2	
		5	CD/CD/CT	1	
CDCT2		1	CT/CD	2	0 2
		2	CT/H	2	
		3	CD/H2	1	
		4	CD/CT2	1	

[a]Multiplicity of all species is 1, Spin of all species is 0, Number of Optical Isomers for all species is 1

[b]The last group for each species is the target group whose group value has been determined in this work. For example the last group shown for CCB2H2 is C/CB2/H2, whose group value has been determined in this work.

Table 2.66 Group Values

Groups	$\Delta H_f^o{}_{298}$ [a]	$S^o{}_{298}$ [b]	Cp300 [b]	Cp400	Cp500	Cp600	Cp800	Cp1000	Cp1500
C/CB2/H2	-1.61	9.69	4.97	6.74	8.17	9.19	10.49	11.46	12.83
Cohen [c]	-6.3								
C/CB/CD/H2	-2.16	8.02	5.45	7.41	8.89	9.93	11.22	12.17	13.68
Cohen [c]	-2.5								
C/CB/CO/H2	-5.96	8.66	5.62	7.66	9.19	10.34	11.75	12.76	0
C/CB/CT/H2	-1.81	9.9	4.36	6.33	7.87	9.04	10.6	11.77	12.53
C/CD2/H2	-2.62	10.59	4.66	6.25	7.66	8.78	10.42	11.71	13.9
Cohen [c]	-4.3								
C/CD/CO/H2	-6.13	10.05	5.16	6.93	8.26	9.3	10.72	11.93	-
C/CO2/H2	-6.08	12.51	3.55	5.54	7.06	8.33	10.01	11.45	-
Cohen [c]	-6.6								
C/CO/CT/H2 [c]	-5.38	10.25	5.28	7.17	8.51	9.57	10.99	12.21	-
Cohen [c]	-5								
C/CT2/H2	3.43	10.83	4.76	6.66	8.12	9.29	10.94	12.24	12.31
CD/CB2	10	-19.04	2.66	4.32	5.38	5.98	6.53	6.72	6.89
Cohen [c]	8								
CD/CB/CD	11.81	-16.87	2.42	3.52	4.33	4.89	5.59	5.87	6.52
Cohen [c]	13								
CD/CB/CT	11.3	-15.42	3.63	4.54	5.72	4.98	5.31	5.56	5.91
CD/CD2	12.19	-12.09	2.24	3.14	4.03	4.8	5.75	5.92	6.29
Cohen [c]	6.6								
CD/CD/CT	11.05	-12.53	3.25	3.79	5	4.49	5.26	5.64	6.11
CD/CT2	15.22	-12.76	4.18	4.4	5.9	4.07	4.62	5.19	5.8

[a] Units in kcal/mol.
[b] Units in cal/mol.K.
[c] Reference 28.

2.5 Summary

Thermodynamic properties of 12 hydrocarbons and three oxygenated hydrocarbons are calculated using density functional method with isodesmic reaction schemes for cancellation of errors in energy. Standard enthalpies of formation, $\Delta H_f^\circ{}_{298}$'s are calculated using only isodesmic reaction schemes based on the B3LYP/6-31G(d). Entropies $S^\circ{}_{298}$ and heat capacities ($C_p(T)$'s ($300 \leq T/K \leq 1500$)) are determined with B3LYP/6-31G(d) optimized geometries and frequencies. Enthalpy, Entropy and $C_p(T)$ properties are determined for C/CD2/H2, C/CB2/H2, C/CD/CT/H2, C/CB/CD/H2, C/CT2/H2, C/CB/CT/H2, C/CO2/H2, CD/CD2, CD/CD/CT, CD/CB/CT, C/CD/CO/H2, C/CO/CT/H2, C/CB/CO/H2, CD/CB/CD, CD/CT2, CD/CB2 groups for use in group additivity. Intramolecular torsion potentials are determined and used for analysis of Cp(T) and S.

CHAPTER 3

CONCLUSIONS

Thermodynamic Properties of CCB2H2, CCBCDH2, CCBCOH2, CCBCTH2, CCD2H2, CCDCOH2, CCO2H2, CCOCTH2, CCT2H2, CDCB2, CDCBCD, CDCBCT, CDCD2, CDCDCT, CDCT2 are calculated using density functional methods with isodesmic reaction schemes for cancellation of errors in the Enthalpy calculations. Standard enthalpy of formation, $\Delta H_f^\circ{}_{298}$ is calculated using isodesmic reaction schemes based on B3LYP/6-31G(d) calculations level. Entropies $S^\circ{}_{298}$ and heat capacities ($C_p(T)$'s ($300 \leq T/K \leq 1500$)) are determined by B3LYP/6-31G(d) optimized geometries and frequencies. Evaluation of data from the isodesmic reaction analysis, results in $\Delta H_f^\circ{}_{298}$ values for CCB2H2 of 42.41 kcal/mol, CCBCDH2 of 34.7 kcal/mol, CCBCOH2 of –13.35 kcal/mol, CCBCTH2 of 74.7 kcal/mol, CCD2H2 of 27.08 kcal/mol, CCDCOH2 of –20.68 kcal/mol, CCO2H2 of -64.88 kcal/mol , CCOCTH2 of 19.72 kcal/mol, CCT2H2 of 112.43 kcal/mol, CDCB2 of 60.86 kcal/mol, CDCBCD of 53.41 kcal/mol, CDCBCT of 94.96 kcal/mol, CDCD2 of 48.68 kcal/mol, CDCDCT of 85.45 kcal/mol and CDCT2 of 131.68 kcal/mol.

Enthalpy, entropy and $C_p(T)$ properties are determined for C/CB2/H2, C/CB/CD/H2, C/CB/CO/H2, C/CB/CT/H2, C/CD2/H2, C/CD/CO/H2, C/CO2/H2, C/CO/CT/H2, C/CT2/H2, CD/CB2, CD/CB/CD, CD/CB/CT, CD/CD2, CD/CD/CT, CD/CT2 groups for use in group additivity. Calculations result in Group Values for C/CB2/H2 of –1.61 kcal/mol, C/CB/CD/H2 of –2.16 kcal/mol, C/CB/CO/H2 of

– 5.96 kcal/mol, C/CB/CT/H2 of – 1.81 kcal/mol, C/CD2/H2 of –2.62 kcal/mol, C/CD/CO/H2 of –6.13 kcal/mol, C/CO2/H2 of –6.08 kcal/mol, C/CO/CT/H2 of –5.38 kcal/mol, C/CT2/H2 of –3.43 kcal/mol, CD/CB2 of 10 kcal/mol, CD/CB/CD of 11.81 kcal/mol, CD/CB/CT of 11.3 kcal/mol, CD/CD2 of 12.19, CD/CD/CT of 11.05 kcal/mol, CD/CT2 of 15.22 kcal/mol.

APPENDIX A

SPREADSHEET FOR CALCULATION OF SPECIES ENTHALPY USING ISODESMIC REACTIONS AND B3LYP/6-31G(d) ENERGY VALUES

This Appendix demonstrates the calculation of the Enthalpy value for each species using an isodesmic reaction, known Enthalpy Values for other species in the reaction except the target species and B3LYP/6-31G(d) Energy Values for all species in the reaction.

Spreadsheet[e] for Calculating Species Enthalpy using Isodesmic Reaction and B3LYP/6-31G(d) Energy Values

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CCD2H2)								
	C7H12(CCD2H2)	+	C2H4	=	C3H6	+	C4H6	
E298[a] →	-195.0653059		-78.4820544		-117.7440033		-155.8172818	
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		4.878107223		26.00382488	
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.01392484	hartree	=	-8.737976348	kcal/mol			
ANSWER[d] →	27.08000846	kcal/mol						

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CCB2H2)								
	C13H12(CCB2H2)	+	C2H4	=	C7H8	+	C8H8	
E298[a] →	-502.1876041		-78.4820544		-271.3064366		-309.3757556	
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		11.95028717		35.10994371	
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.01253372	hartree	=	-7.865034637	kcal/mol			
ANSWER[d] →	42.38536552	kcal/mol						

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CCBCDH2)								
	C9H10(CCBCDH2)	+	C2H4	=	C7H8	+	C4H6	
E298[a] →	-348.6268569		-78.4820544		-271.3064366		-155.8172818	
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		11.95028717		26.00382488	
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.01480716	hartree	=	-9.291640972	kcal/mol			
ANSWER[d] →	34.70585303	kcal/mol						

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CCT2H2)								
	C5H4(CCT2H2)	+	C2H4	=	C4H4	+	C3H4	
E298[a] →	-192.6469954		-78.4820544		-154.6072265		-116.5380024	
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		70.50669431		44.31166483	
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.01617914	hartree	=	-10.15257214	kcal/mol			
ANSWER[d] →	112.4310313	kcal/mol						

Spreadsheet[e] for Calculating Species Enthalpy using Isodesmic Reaction and B3LYP/6-31G(d) Energy Values (Continued)

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CCBCT)

	C9H8(CCBCT)	+	C2H4	=	C8H8	+	C3H4
E298[a] →	-347.4202569		-78.4820544		-309.3757556		-116.5380024
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		35.10994371		44.31166483
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.01144678	hartree	=	-7.182968918	kcal/mol		
ANSWER[d] →	74.06467746	kcal/mol					

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CCO2H2)

	C3H4O2(CCO2H2)	+	C2H4	=	C2H4O	+	C3H4O
E298[a] →	-267.0036997		-78.4820544		-153.7147535		-191.784604
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		-40.7982804		-20.07648245
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.01360344	hartree	=	-8.536294634	kcal/mol		
ANSWER[d] →	-64.87836822	kcal/mol					

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CDCD2)

	C6H8(CDCD2)	+	C2H4	=	C4H6	+	C4H6
E298[a] →	-233.1444265		-78.4820544		-155.8172818		-155.8172818
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		26.00382488		26.00382488
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.00808276	hartree	=	-5.072012728	kcal/mol		
ANSWER[d] →	44.5397625	kcal/mol					

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CDCDCT)

	C6H6(CDCDCT)	+	C2H4	=	C4H6	+	C4H4
E298[a] →	-231.9400993		-78.4820544		-155.8172818		-154.6072265
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		26.00382488		70.50669431
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.0023547	hartree	=	-1.477597797	kcal/mol		
ANSWER[d] →	85.44821699	kcal/mol					

Spreadsheet[e] for Calculating Species Enthalpy using Isodesmic Reaction and B3LYP/6-31G(d) Energy Values (Continued)

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CDCBCT)							
	C10H8(CDCBCT)	+	C2H4	=	C8H8	+	C4H4
E298[a] →	-385.4979317		-78.4820544		-309.3757556		-154.6072265
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		35.10994371		70.50669431
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.00299602	hartree	=	-1.88003251	kcal/mol		
ANSWER[d] →	94.95677053	kcal/mol					

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CCDCO)							
	C4H6O(CCDCO)	+	C2H4	=	C3H6	+	C3H4O
E298[a] →	-231.0352988		-78.4820544		-117.7440033		-191.784604
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		4.878107223		-20.07648245
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.01125422	hartree	=	-7.062135592	kcal/mol		
ANSWER[d] →	-20.67613963	kcal/mol					

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CCTCO)							
	C4H4O(CCTCO)	+	C2H4	=	C3H4	+	C3H4O
E298[a] →	-229.8277603		-78.4820544		-116.5380024		-191.784604
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		44.31166483		-20.07648245
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.01279176	hartree	=	-8.026957318	kcal/mol		
ANSWER[d] →	19.7222397	kcal/mol					

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CCBCO)							
	C8H8O(CCBCO)	+	C2H4	=	C7H8	+	C3H4O
E298[a] →	-384.5973246		-78.4820544		-271.3064366		-191.784604
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		11.95028717		-20.07648245
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.01166168	hartree	=	-7.317820817	kcal/mol		
ANSWER[d] →	-13.34827446	kcal/mol					

Spreadsheet[e] for Calculating Species Enthalpy using Isodesmic Reaction and B3LYP/6-31G(d) Energy Values (Continued)

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CDCBCD)								
	C10H10(CDCBCD)	+	C2H4	=	C4H6	+	C8H8	
E298[a] →	-386.7049815		-78.4820544		-155.8172818		-309.3757556	
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		26.00382488		35.10994371	
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.00600158	hartree	=	-3.766051466	kcal/mol			
ANSWER[d]→	52.33992006	kcal/mol						

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CDCT2)								
	C6H4(CDCT2)	+	C2H4	=	C4H4	+	C4H4	
E298[a] →	-230.7272954		-78.4820544		-154.6072265		-154.6072265	
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		70.50669431		70.50669431	
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.0051032	hartree	=	-3.202309032	kcal/mol			
ANSWER[d]→	131.6757977	kcal/mol						

Isodesmic Reaction to find $\Delta H_f^\circ{}_{298}$(CDCB2)								
	C14H12(CDCB2)	+	C2H4	=	C8H8	+	C8H8	
E298[a] →	-540.2643905		-78.4820544		-309.3757556		-309.3757556	
$\Delta H_f^\circ{}_{298}$[b] →			12.5399		35.10994371		35.10994371	
$\Delta H^\circ{}_{rxn,298}$[c] →	-0.00506634	hartree	=	-3.179179013	kcal/mol			
ANSWER[d]→	60.85916643	kcal/mol						

[a]E298 represents the B3LYP/6-31G(d) energy of the species (ZPVE and thermal correction are considered)

[b]$\Delta H_f^\circ{}_{298}$ represents the Enthalpy of formation of the particular species

[c]$\Delta H^\circ{}_{rxn,298}$ represents the Heat of reaction

[d]Answer in each case is the $\Delta H_f^\circ{}_{298}$ of the target species.

[e]Note that since 1 Hartree = 627.51 kcal/mol the energy values shown in Hartrees are important to 6 significant figures past the decimal, while the Enthalpy values shown in kcal/mol are important to 2 significant digits after the decimal.

APPENDIX B

REFERENCE GROUP VALUES USED TO CALCULATE THE GROUP VALUES FOR TARGET GROUPS

This Appendix contains the following table:

Table A-1 Reference Group Values

This table gives the group values for different groups used in the Group Additivity calculations to determine Group Values for the target groups in this work.

Table A-1 Reference Group Values

Group	$\Delta H_{f\,298}^{o}$ [a]	S^{o}_{298} [b]	Cp300[b]	Cp400	Cp500	Cp600	Cp800	Cp1000	Cp1500
CB/C	5.51	-7.69	2.67	3.14	3.68	4.15	4.96	5.44	5.98
CB/CD	5.8	-7.8	3.59	3.97	4.38	4.72	5.28	5.61	5.75
CB/H	3.3	11.53	3.24	4.44	5.46	6.3	7.54	8.41	9.73
CD/C/H	8.59	7.97	4.16	5.03	5.81	6.5	7.65	8.45	9.62
CD/CD/H	6.78	6.38	4.46	5.79	6.75	7.42	8.35	9.11	10.09
CD/H2	6.26	27.61	5.1	6.36	7.51	8.5	10.07	11.27	13.19
CO/C/H	-29.4	34.9	7.03	7.87	8.82	9.68	11.2	12.2	-
CT/C	27.3	6.35	3.13	3.48	3.81	4.09	4.6	4.92	6.35
CT/CD	27.9	6.43	2.57	3.54	3.5	4.92	5.34	5.5	5.8
CT/H	27.2	24.7	5.28	5.99	6.49	6.87	7.47	7.96	8.85

[a]Group Values for Enthalpy from Reference 28, Units kcal/mol

[b]Group Values for Entropy and Heat Capacity(300K – 1500K) from Reference 33, Units cal/mol/K

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